Carolina Infante da Câmara dos Reis Peixe

Licenciada em Conservação-Restauro

The *Passos Manuel* high school glass crystal models: Condition assessment and analytical characterization

Dissertação para obtenção do Grau de Mestre em
Conservação e Restauro, especialização em Conservação e Restauro

Orientador: Professora Doutora Inês Alexandra Ramalho Coutinho,
Professora Auxiliar,
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26 de Novembro, 2019

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UNIVERSIDADE NOVA DE LISBOA

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Aos meus pais!

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Abstract

Glass crystal models are didactic instruments used since the 19^{th} century to support crystallography classes. Their implementation in Portugal occurred during the end of the 19^{th} century with the appearance of the Portuguese *Liceus*. In these institutions, it was important that classes were not exclusively taught recurring to school textbooks. Following this, high schools, universities, and polytechnics were gradually provided with teaching collections to ensure that students have a tridimensional vision of what was taught in science education. Therefore, this kind of models are an important material evidence of teaching methodologies of mineral and geology science in the 19^{th} and 20^{th} centuries.

The *Passos Manuel* high school, in Lisbon, owns a significant collection of scientific heritage, part of which is currently on a long-term loan at the National Museum of Natural History and Science from the University of Lisbon, which includes a set of 98 glass crystal models. Apart from glass, these models are composed by paper/textile adhesive tapes, adhesives, cardboard, textile lines and metal nuts and screws. On a first approach, some models seem to have been subjected to repairing processes, presenting different conservation conditions.

This study aims to perform an assessment of the current condition of the *Passos Manuel* high school glass crystal models collection, as well as its material characterization. To achieve these main objectives, a custom condition scale for glass crystal models was developed and the collection characterization was done based on portable equipment (p-XRF), or by collecting small samples further analyzed using optical microscopy and ATR-FTIR techniques. This study represents an initial approach for the development of a conservation and restoration methodology for glass crystal model collections.

Keywords: glass crystal models; didactic collections; scientific and collections heritage; conservation condition diagnose; material characterization.

Resumo

Modelos cristalográficos de vidro são instrumentos didáticos usados desde o século XIX para dar apoio a aulas de cristalografia. Em Portugal, estes modelos foram implementados no final do século XIX, com o aparecimento dos primeiros liceus portugueses. Nestas instituições havia a preocupação que as aulas não fossem exclusivamente dadas através de manuais escolares. Assim, escolas secundárias, universidades e politécnicos começaram a ser gradualmente equipados com coleções de ensino, de forma a garantir que os alunos tivessem uma visão tridimensional do que era lecionado relativamente a diferentes ciências. Por esta razão, este tipo de modelos são um marco das metodologias de ensino que eram aplicadas na mineralogia e geologia durante os séculos XIX e XX.

A Escola Básica e Secundária Passos Manuel, em Lisboa, tem uma coleção significativa de instrumentos científicos, parte da qual atualmente em depósito no Museu Nacional de História Natural e da Ciência da Universidade de Lisboa, que inclui uma coleção de 98 modelos cristalográficos de vidro. Para além do vidro, estes modelos são compostos por fitas adesivas de papel/têxtil, adesivos, cartão, linhas têxteis e parafusos e porcas de metal. Numa primeira abordagem, alguns modelos aparentam ter sofrido algum tipo de processo de intervenção e a coleção aparenta diferentes estados de conservação.

Este estudo tem como objetivos fazer uma avaliação do estado de conservação da coleção de modelos cristalográficos de vidro da Escola Básica e Secundária Passos Manuel, assim como a sua caracterização material. De forma a alcançar estes objetivos, uma escala de estado de conservação personalizada foi desenvolvida especificamente para modelos cristalográficos de vidro e a caracterização da coleção foi feita com base em equipamentos portáteis (p-XRF), ou através da análise de amostras por microscópio ótico ou FTIR-ATR. Este estudo representa uma abordagem inicial que serve como base para o desenvolvimento de uma metodologia de conservação e restauro para modelos cristalográficos de vidro.

Palavras-chave: modelos cristalográficos de vidro; coleções didáticas; colecções e património científico; diagnóstico de estado de conservação; caracterização material.

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List of Symbols and Abbreviations

3D	Tridimensional
Al_2O_3	Aluminum oxide
ATR-FTIR	Fourier-transform Infrared Spectroscopy in Attenuated Total Reflectance
C	Carbon
C=O	Carbon and oxygen double bond
Ca	Calcium
ca.	Circa
CAMEO	Conservation and Art Materials Encyclopedia
CaO	Calcium oxide
C-H	Carbon and hydrogen bond
CHx	Hydrocarbon groups
CMoG B	Corning Museum of Glass standard B
CMoG D	Corning Museum of Glass standard D
C-O	Carbon and oxygen bond
Fe_2O_3	Iron (III) oxide
H	Hydrogen
H_2SO_4	Sulfuric acid
HCl	Hydrochloric acid
K	Potassium
K_2O	Potassium oxide
Mg	Magnesium
MT	Microchemical test
MUHNAC	Museu Nacional de História Natural e da Ciência
N	Nitrogen
N-H	Nitrogen and hydrogen bond
O	Oxygen
OH	Hydroxyl group
O-H	Oxygen and hydrogen bond
OM	Optical microscope
PRISC	Portuguese Research Infrastructure of Scientific Collections
p-XRF	portable X-ray fluorescence spectroscopy
Rh	Rhodium

S	Sulfur
Si	Silicon
SiO	Silicon monoxide
Si-O	Silica and oxygen bond
SiO_2	Silicon dioxide
Si-O-Si	Silicon and oxygen and silicon bond
SO_4^{3-}	Sulphate group
TAPPI	Technical Association of the Pulp and Paper Industry
U	Uranium
UL-DEPXXXX	Inventory attributed number to deposit objects in MUHNAC

1. Introduction

Scientific heritage collections are present in many institutions, such as schools, universities, hospitals, to name a few [1]. The majority of these historical collections and their preservation are responsibility of said institutions and should be performed in their installations. However, not all of them have well documented and established conservative procedures to properly maintain this scientific heritage *in situ* [1]. Since 2007, the *Museu Nacional de História Natural e da Ciência* (MUHNAC) started to promote research initiatives into methods to preserve these types of collections, with the main objective of providing the needed preservation guidelines to maintain, *in situ,* the institutions' scientific heritage [1]. Unfortunately, *in situ* preservation of these collections is not always possible due to the absence of proper conditions in said institutions [1]. Only in substantial lack of conditions and urgent need by the institutions to properly preserve their collections, the MUHNAC chooses to accept the collections on a long-term loan, to protect the scientific heritage at risk [1]. This is the case of the *Passos Manuel* high school glass crystal models collection. Due to a considerable reform in this high school building, the conditions to maintain this collection locally were not met; therefore, MUHNAC accepted the *Passos Manuel* high school collection on a long-term loan.

Implementing preservation guidelines that can, ultimately, be passed on to the *Passos Manuel* high school representatives, to ensure that this collection is properly maintained *in situ* is a complex process that needs to follow several steps.

Firstly, it is necessary to assess the current conservation condition of the collection, to better perceive the starting point and more urgent needs to address. These scientific collections have two main crucial periods in their lifetime that are important to comprehend: the first is the actual time when the models were actually used (or not), which translates in use marks in these objects, originated whether from the daily use of the individual object or possible repairs needed due to this usage; the second is the period after usage that, without proper care, may also have left the models with other consequences that may have contributed to the object's deterioration [2].

Next, a clear characterization of the models' materials and components is crucial to understand the materials present. This allows to fully characterize the collection and enables the identification of the main problems associated with the conservation of the materials that constitute the models. Only after these two steps, it is possible to start designing and testing conservation and restoration procedures that serve the needs of glass crystal models collections and their inherent problems. These procedures will, ultimately, result in a consolidated conservation and restoration methodology, providing guidelines and tools to maintain these types of collections, similarly to the objectives of the MUHNAC research initiatives with different institutions.

The objectives of the present work are deeply associated with the first two steps of the complex process mentioned previously, applied to the *Passos Manuel* high school glass crystal model collection.

The first is assessing the current conservation condition of the collection. To do so, it is necessary to understand what is crystallography and the role that these models had in the study of crystallography science. This is crucial to perform an accurate diagnose of the conservation condition of this collection, which will in turn provide knowledge about the two lifetime periods of these objects. Despite the aim of this assessment being the clarification of the collection's overall condition, this shall be achieved by performing the assessment for each individual model, evidencing the individual needs of each object.

The second is to perform an exhaustive compositional characterization of the glass crystal model of the glass crystal models collection. This will allow to understand the different materials used in glass crystal models and distinguish the original materials from repairs. The results of both approaches coupled together will allow to obtain an accurate assessment of the conservation state of these objects, establishing a baseline for the future work to be developed.

1.1. Crystallography and glass crystal models

Crystallography is the branch of science that studies the structure and properties of crystals, that exists as an individual subject since the diffracted X-rays were discovery. Despite its individual scope, this subject has always been connected with mineralogy and geology studies. To comprehend the evolution of this science and the appearance of the glass crystal models it is necessary to go back to the late 16th century where the principal results of crystals' studies were mostly presented by books on minerals and mining industries [3].

1.1.1. The origins of crystallography

Minerals were classified and divided by their physical characteristics for the first time in Georgios Agricola's (1494-1555) work, *De Natura Fossilium*, in 1546 [3]. His book came to demystify that minerals had superpowers, presenting them with their natural properties and giving relevance to the minerals' different geometric forms [3]. Agricola's return 10 years later (1556) with a new publication, *De Re Metalica*, mainly focused on mining techniques, but also extends the research presented in *De Natura Fossilium*, by establishing a relation between the minerals' physical characteristics and the different crystalline mineral forms [3]. But it is only in 1568 that Crystallography takes a huge advance when Wentzel Jamitzer (1508-1586), a master goldsmith and German jeweller, that publishes his work results at *Perspectiva Corporum Regularium* that consisted on the preparation of 140 models with geometric shapes [3]. After that, in 1621, comes the discovery of light's refraction law when it crosses a liquid by Willebrord Snel (1580-1626). This would be of great importance to Crystallography science, although it was only published in Issac Vossius' (1618-1689) *De Lucis Natura et Proprietate* one year later, in 1622 [3].

1.1.2. Crystal models

Despite all the developments during the 16^{th} and 17^{th} centuries, it was only in the 18^{th} century that crystal models were referred in connection with mineralogy [4]. This occurred after 1735, when Carolus Linneaus (1707-1778), a Swedish naturalist, prepared wood crystal models [4]. However, it was not until the 1780s that these models began to be intertwined with crystallography [4].

In 1772, Romé de l'Isle (1736-1790) published his first edition of the famous *Essai de Cristallographie*, where crystallography and mineralogy were finally defined as a science. Along with it, and with the need to create a way to visualize crystals tridimensional, this book included what the author called *developments*, an illustration template to cut and construct a tridimensional (3D) crystal shape [4]. With the success of the first edition, a second one was released in 1783, this time with an extended version of 483 illustrations of crystals and minerals from the author's own private collection. In this second edition, Romé de l'Isle created a prize to send to their subscribers: a 3D terracotta model (Figure 1a), made with the help of two of his students, Claude Lemina and Arnould Carangeot.

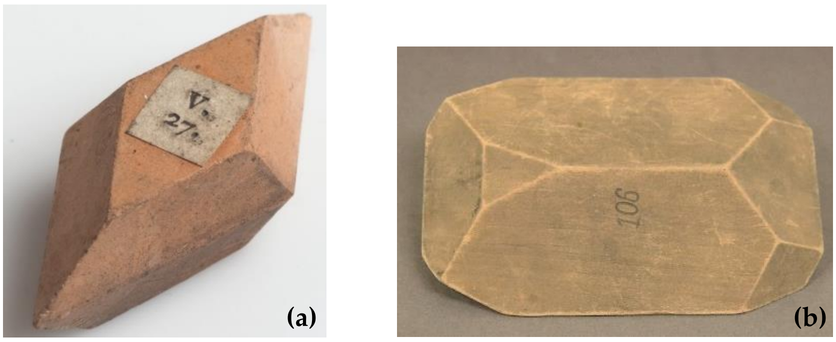


Figure 1. 3D models: **(a)** Terracotta prize model from Romé de l'Isles [2]; **(b)** Wood model from a box (UL-DEP1325) from Passos Manuel high school collection, currently in MUHNAC's technical storage (Picture: MUHNAC, ®C. Peixe, June 2019).

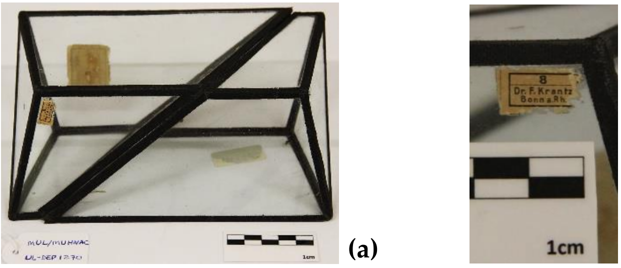
Arnould Carangeot developed a goniometer[1] prototype, which increased the measurement of inter planar angles close to half of a degree and that had been possible due to the use of terracotta models instead of natural crystals [3] [4].

Around 1800, terracotta models were replaced by wooden ones (Figure 1b). These were better, comparing with the terracotta ones, in the sense that these allowed for softer faces, more defined edges and a greater rigour in the creation of angles [4]. Since the introduction of these models by Romé de I'Isle, the quantity of their production increased, being simultaneously required as models of education and minerals' collection [4].

Throughout the 19^{th} century, the importance of collections in science education led to the emergence of a global industry, with greater preponderance in France, Germany and England [5]. The creation of the

[1] A goniometer is a measure angles instrument, used in specific to measure body joint angles [33].

Krantz company in Bonn, in 1833, fits the increase in demand and productions of these materials. The company was established by Adam August Krantz, who started the production of crystallographic models in glass (Figure 2) [6].



(a) (b)

Figure 2. Glass crystal model (UL-DEP1270) from *Passos Manuel* high school collection in the MUHNAC's technical storage **(a),** model showing label from Krantz Company; **(b)** detail of the label from Krantz Company.
Pictures: MUHNAC, ®C. Peixe, June 2019

Nevertheless, it is believed that crystal models, along with other teaching instruments to support classes, had an increasing availability in school's education in the 20th century [5]. This typology of models was introduced in Portugal from different manufacturers, as Émile Deyrolle, Robert Bendel, Louis Auzoux and Krantz Company, companies from France, England and Germany [5]. In Portugal, in the 1960s, models started to be substituted and acquired from different local distributors and providers of didactic materials, such as Tecnodidática, FOC, Nucleon, Telecol, J. Morais Rocha, Barral, Comundo, amongst others national distributors [5].

According to I. Gomes (2014), between the years of 1966 and 1972, many requisitions of crystal models had been made by schools all over the country through the different national distributors mentioned above [5]. Amongst these crystal models, the most required ones were made from wood and plastic. This was probably due to the fragility that the glass model's present and, possibly, because models from other materials were easier, and possibly cheaper to acquire [5]. In relation to glass crystal models, these are also found in schools, in sets of 25 to 100 models, namely high schools, polytechnics and universities from north to south of Portugal [5]. Besides the models from the *Passos Manuel* high school focused in the present work, there are models at *Pedro Nunes* high school, *Colégio Militar, Colégio do Sagrado Coração de Maria* [2] in Lisbon, amongst others, not only in Lisbon but also across the country [5]. These collections started to lose their interest in the teaching methodologies with the appearance of new technologies, such as film projectors, internet and easy access to information and images, making it cheaper to show these kinds of models through images [5].

1.1.3. Glass crystal models worldwide

Besides Portugal, glass crystal models also exist throughout the world. Through the RETE community of the History of Science Museum[2], several queries were submitted in the hopes to obtain more accurate

[2] Link to this community: https://www.hsm.ox.ac.uk/

information about the existence of these models. The main questions were: "*Are you familiar with any historical or conservation studies about Krantz models, or any crystallography models?*" and "*Can you direct me to some specific literature, or websites of interest?*". The information that was possible to acquire through the queries submitted to the RETE community is presented next.

The first main point highlighted is that no specific work focused on glass crystal model's conservation had been made or communicated, as far as it was possible to collect. As far as the existence of other samples of models, in the Nacional Museum of Scotland, the models in storage are from wood, metal, porcelain, plastic and glass. There are 2 from Krantz company and 11 manufactured by Samuel Highley[3] (1826-1900) around 1854 [7]. Utrecht University and Leiden University in the Netherlands' also had glass crystal models, that, presently, are believed to be stored at the Utrecht University Museum [8]. In the Utrecht University, as communicated, there was an occasion that a model was repaired by cutting a new window out of window glass which was fixed with narrow tape over the ribs [8]. This information reinforces the possibility of these models being repaired by teachers, students or other technicians present in these institutions [2]. The Mineralogy Museum of Strasbourg has 2885 wood crystal models, but only 17 are made of glass [9]. These are not from Krantz Company but from F. Thomas company from Siegen, which was older than Krantz company [9]. The technological University of Bergakademie Freiberg in Germany has 20 glass crystal models from Krantz company and, finally, the German Museum in Munich had 8 [9].

Overall, the information obtained suggests that the models from Krantz's company were the most popular ones, but not the only ones existing; possibly, other companies produced glass crystal models; the last suggestion should be further investigated to obtain a more informed confirmation. Apart from this, it was still possible to identify the variety of materials in which these models were produced; models that contained glass as a constituent material were fewer in numbers.

1.2. *Passos Manuel* high school: brief historic context and recent developments on the preservation of its scientific heritage

During the 19th century, most exactly during the liberal revolution in 1820 and onwards, Portugal started to reform the public instruction, increasing the science subjects and implementing collections of natural history in high schools. Since there was a concern that classes should not be supported only through school textbooks, but also by the 3D visualization of the taught subjects, crystal models provided a solution for this need: as they represent the organization inside the crystals, allowing the students to

[3] Born in 1826, Samuel Highley worked with his father at a shop specialized in Medical books [35]. After his father's death, he continues to publish scientific and medical books [35]. Had been the first to sell microscopes, in 1853, and, in 1854, started to focus his shop in microscopy, geology and chemistry sciences and instruments [35].

visualize this and to better comprehend it [5]. In 17th November 1836, Manuel da Silva Passos[4], known by Passos Manuel, publishes the *Plano dos Liceus Nacionais*, with the vision of reforming the education in Portugal and changing it into the standards of the European high schools from the 20th century, such as the model of French *lycées* and Germany *gymnasien* [5]. Therefore, he founded in the same year the first *Liceu* in Portugal, the *Liceu Nacional de Lisboa,* later called the *Liceu Passos Manuel* [5] [10].

In 1895, through Jaime Moniz's[5] reform, the discipline of natural history was integrated into the curriculum of high school education and, despite some criticisms regarding the lack of materials to do so, it is known that, at that time, more than 70% of the high schools had zoological, botanical, geological and mineralogical collections [5].

2007 marks the beginning of new reforms in schools of Portugal. In 21st of February 2007, the Ministry of Education approves the modernization program destined to high schools by *Parque Escolar, E.P.E.* [11]. In *Passos Manuel* high school, the intervention takes place from April 2007 to April 2010, encompassing previous studies, licences, project execution and buildings reconstruction, as well as the need to protect and preserve all the scientific collections of the high school [12]. As mentioned, the MUHNAC has a long tradition in supporting the preservation of scientific heritage, mainly in Lisbon institutions and in its own university [1], and more recently across the country, through the creation of the PRISC[6] – Portuguese Research Infrastructure of Scientific Collections in 2013 –, under its management.

Since 2007, the MUHNAC has been providing regular technical conservation support to scientific heritage to several institutions, covering nowadays ca. 30 institutions supported by this initiative, including the *Passos Manuel* high school [1]. The program promotes the cooperation between the museum and schools, in order to better preserve and safeguard the historical-scientific heritage [1]. It was under this scope and due to the *Parque Escolar* intervention, that, in 2008, part of the *Passos Manuel* scientific collections were deposited into the MUHNAC's storages for a long-term loan. And thus, here is where the collection of 98 glass crystal models, the object of this study, is currently preserved.

[4] Born in 1801, Manuel da Silva Passos, graduated in law in the University of Coimbra, where he starts to gain interest in the political world [12]. He assumes the direction of the September Revolution in 1836, promising to lead in the interests of the country [12]. Simultaneously, he published some legislative works featured in the administrative code from 31st of December 1836, and a large teaching reform, setting *Liceus* in almost every district capital and funding the firsts technical teachings, the conservator of arts and crafts of Lisbon [12]. Manuel da Silva Passos would die in 1862 with his name in the history as one of the biggest figures from the 19th century liberalism [12].

[5] Born in 1837, Jaime Moniz, graduated in law in the University of Coimbra [34]. He was a Portuguese politic and intellectual with distinction in the area of education, leading the 1894-1895 high schools reform which had influenced the development of teaching methods up until the 1930 decade [34].

[6] Link to the PRISC network: https://www.prisc.pt/

1.2.1. Glass crystal models case-study – First approach to its characterization[7]

To properly characterize the glass crystal models from the *Passos Manuel* high school collection it was necessary, on a first approach, to categorize the models in respect to their typologies, constituent materials and any characteristics that could help with the identification of the models' provenance.

The case-study of this collection was already explained in the publication: "*Glass Crystal Models: A first Approach to a Hidden Treasure of Teaching and Scientific Heritage*" [13] presented in Appendix I. To achieve this, two main steps were followed. First, a macro observation was performed: this consisted in making a first characterization of the 98 models, reviewing all the components that constitute them and their main characteristics, resulting in a separation by typologies. Then, a comparison between the reviewed characteristics and catalogues for this type of models was performed. This step aimed to create a correlation, to the possible extent, the models from the *Passos Manuel* high school collection with the ones found in these catalogues, to have a more precise identification of the models' provenance. The main aspects of this first approach are presented next.

In the beginning of this study, half of the *Passos Manuel* glass crystal model's collection was still packed in a bubble wrap (Figure 3) as they came from the school, with a register number label, also from the *Passos Manuel,* correspondent to the list of models that entered the museum from their collection.

Figure 3. Glass crystal models from *Passos Manuel* high school packed in bubble warp in MUHNAC's Technical Storage | Picture: MUHNAC, ®C. Teixeira, September 2018

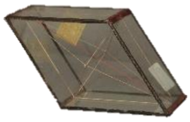
In 13th of October, the glass crystal models collection started to be inventoried by Mrs. Manuela Mineiro, a former physics teacher in *Passos Manuel* high school and current MUHNAC's Volunteer, who helped packing and organizing the collections in *Passos Manuel* high school before moving to the museum.

The glass crystal models collection integrates 98 models composed mostly by glass, but also by other components with different materials such as: paper and cardboard, textile threads, adhesives and

[7] This chapter is part of Peixe, C. *et al,* Glass Crystal Models: A first Approach to a Hidden Treasure of Teaching and Scientific Heritage, Heritage, Lisbon, Portugal (2019) [13] presented in Appendix I

paper/textile adhesive tapes and metal nuts and screws, each one with different purposes that gives models different typologies, presented on Table 1.

Table 1. Consistent typologies identified in the *Passos Manuel* glass crystal models collection (Pictures: MUHNAC, ®C. Peixe, February 2019).

Typology Reference	Brief Description	Qty.	Example
A	Glass model with textile lines inside, representing the crystal axes	63	 UL-DEP1268
B	Glass model with interior model of cardboard representing the crystal axes	24	 UL-DEP1269
C	Glass model with two rotating parts, showing the ability of the crystal to acquire different forms	8	 UL-DEP1309
D	Glass models that do not fit any of the characteristics mentioned above, probably due to previous repairs	3	 UL-DEP1244

Besides the characteristic materials of the different typologies of models from Table 1, there are other materials present in the models: adhesive to join the edges of the glass faces, paper/textile adhesive tapes to give support to the joining edges, and a few paper labels with printings and/or manuscript ink, all with different correspondences and attached at different moments in time.

Although models may be divided and fit in the four categories as evidenced in Table 1, during their first observation, a label from Krantz company was identified in 4 glass crystal models. So, since the first classification gives no clue to its production provenance and it was possible to buy sets of models with characteristics of types A, B and C, it was necessary to reorganize them and see other differences beyond those mentioned in Table 1. The paper adhesive tapes that join the glass edges are not the same for all the models, neither in colour nor in width and texture; they came in black, blue, red and/or light yellow and some look like a textile, while others appear to be a plastic material. The paper models inside the glass models can be of the same colour (off-white paper colour), or can have two colours, alternated sides, one off-white paper colour and the other black or *Bordeaux*. The textile lines inside the glass models can also have different colours, ranging from red, orange, yellow, green and blue. From the 98 models it was possible to identify 1 model with a cleavage interior plan made of glass (Figure 4a). For some models, the different features identified – either different coloured paper adhesive tapes, or the presence of gypsum

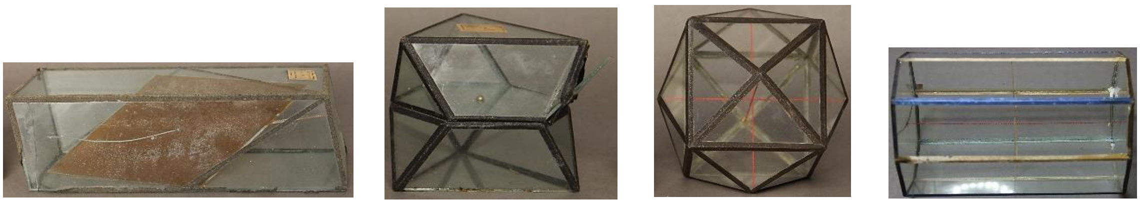
– can probably be related with later interventions made overtime due to usage of the objects. Also, it was noticed that 4 of the 98 models reveal labels from the Krantz company.

Combining and analysing the different characteristics mentioned above and matching the models with Krantz's Company catalogues 29 and 29b, dated 1925 and 1936 respectively [14], it was possible to suggest a provenance for different types of models within the collection, as presented in Table 2.

Table 2. Proposal for a provenance scheme of the *Passos Manuel* glass crystal models collection.

Model Reference	Provenience	Qty.
I	Krantz Company Models	85
II	Modified Models	12
III	School-manufactured Models	1

From the total 98 models, 85 are possibly from Krantz Company with different year of production. Four examples of these models are shown in Figure 4.



(a) **(b)** **(c)** **(d)**

Figure 4. Glass crystal models from *Passos Manuel* high school collection in the MUHNAC's technical storage proposed to be from Krantz's company different generation: **(a)** Glass crystal model (UL-DEP1321) with inner glass plan; **(b)** Glass crystal model (UL-DEP1309) with metal nuts and; **(c)** Glass crystal model (UL-DEP1240) with inner textile lines in red; **(d)** Glass crystal model (UL-DEP1280) with inner textile lines in red and yellow and blue red and black adhesive tapes. Pictures: MUHNAC, ®C. Peixe, February 2019

The first models reveal only black paper/textile adhesive tapes (Figure 4a and 4b), with different textures and integrity (possibly indicating different generations). This contrasts with the coloured paper/textile adhesive tapes (red and blue) from Figure 4d. Referring to inner textile lines, the evolution occurred from one colour (Figure 4c) to several colours (Figure 4d) such as red, green, yellow and orange. So, among these 85 models it is possible to notice the evolution of these characteristics and divide them into four distinct types (Figure 4) that could represent four generations of glass crystal models made by the Krantz Company, possibly acquired in different moments [4] [14].

For the remaining 13 models of *Passos Manuel* high school collection, it is not possible to visually assume and recognize any characteristic from the original Krantz models, due to the heavy alterations in its conditions. One of these 13 models, UL-DEP1249, is believed to be a school-manufactured model, for several reasons: the paper/textile adhesive tapes are present in two different shades of green (which is never present in any other model, particularly in the Krantz company models); the inner paper/cardboard model is substantially different from the ones present in the other models, portraying two different shades of white; the inner paper/cardboard model is supported by two wooden pieces, similar to toothpicks, possibly included to prevent this component from moving – this supporting technique is not found in none of the other models (particularly in the ones from Krantz company); lastly, the UL-DEP1249 model contains a label with a person's name, possibly the name its manufacturer.

2. Methodology

For the development of the proposed study, the methodology presented in Figure 5 was adopted.

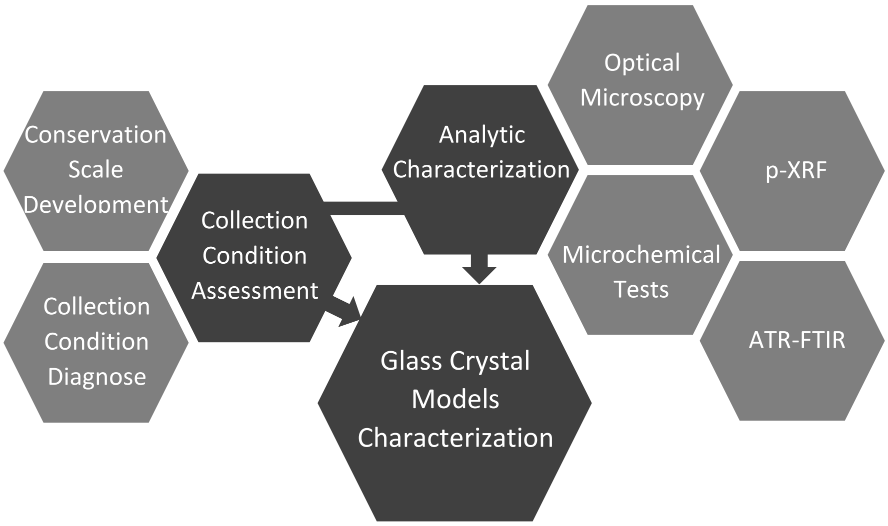


Figure 5. Scheme of the methodology adopted in the present study

To obtain the glass crystal models characterization, two main methods were considered. The collection's conservation condition needed to be evaluated in greater detail and the analytical characterization of the models needed to be further identified using the different techniques presented in Figure 5. These two steps would culminate in the glass crystal model collection from *Passos Manuel* high school full characterization by assessing the conservation conditions of the individual models and the global collection, as well as all attempting the general identification of the original materials present in the models.

After the initial analysis presented in Chapter 1, the first step was to properly conduct the collection conservation condition diagnostic. This was divided in two sub-steps: first, a conservation scale was developed (Chapter 2.1) that consisted in comparing the scale used in the MUHNAC with references present in specific literature [15] [16], with the aim of developing a scale more adapted simultaneously not only to the reality of glass crystal models individually, but also that could evidence the conservation condition of the overall collection. Each of the 98 models were evaluated according to the developed scale, to further complement the macro observation already performed in Chapter 1.2.1, emphasizing the current physical and chemical alterations to its conditions. The main results of this assessment are presented in greater detail in Chapter 3.1.

The analytic characterization was made using four different analytical techniques with results being presented in Chapter 3.2. The first technique used was the optical microscope (OM) with the objective of observing paper and textile fibres from paper/textile adhesive tapes from the model's edges and from the inner textile lines. Then, the inner cardboard/paper models and labels, suspected to be constituted by industrial paper due to the time of production of the models and its direct connection with the Krantz company production, as presented previously in chapter 1.2.1, were analysed by microchemical tests (MT) to see if specific materials were present in their composition, such as lignin, alumen salts and/or rosin, yielding the quality of the papers used to build the models. To analyse the glass, a portable X-ray fluorescence spectroscopy (p-XRF) equipment was used. And finally, it was necessary to analyse the adhesives used in different parts of the models, such as the edges of glass, paper/adhesive tapes, labels, and repairs. To do so, Fourier-transform infrared spectroscopy in attenuated total reflectance mode (ATR-FTIR) equipment was used to characterize the adhesives present in the models.

2.1. Collections condition assessment

The procedure to perform the collection's condition assessment of the *Passos Manuel* high school glass crystal model collection was comprised in several steps. This procedure was applied to each model individually, to obtain a full evaluation of each model's current condition; reviewing all these evaluations in a consolidated perspective, this procedure allows to, ultimately, assess the global collection's condition. As mentioned previously, the main results of this assessment are presented in Chapter 3.1.

Firstly, the MUHNAC's internal condition scale designed to evaluate history of science artefacts, developed in 4 states – good, reasonable, inadequate and poor – was considered. After consulting specific literature [15] [16], the need to create a costume scale for glass crystal models seemed more appropriate. This was due, as mentioned before, particularly to the specificity of this collection materiality, but also, bearing in mind that to larger collections or diverse – which are common in schools – this condition scale could be simpler to be applied, specially by non-conservators. So, an intermediate condition scale with 3 states – good, fair and poor – and 4 parameters to be evaluates using the mentioned states – lacunas, chemical alterations, physical alterations and object interpretation – was created and is presented in Table 3.

Table 3. Proposed condition scale for the assessment of a glass crystal model

	Lacunas	Other Physical Alterations	Chemical Alterations	Object Interpretation
Good	< 35%	5 / 4	5 / 4	Yes
Fair	≥ 35% and < 65%	4 / 3 / 2	4 / 3 /2	Yes
Poor	≥ 65%	2 / 1	2 / 1	No

Each parameter should be interpreted as follows:

- **Lacunas:** Represents the material loss in each component of the models, whether being glass, paper or adhesive, and should be evaluated as a percentage – the whole object corresponds to 100%, meaning the percentage of the lacuna represents the portion of the material that is missing. These percentages must be attributed in gaps of 5%, since this evaluation represents an estimation based on macroscopic visualization of the object; a more in-depth evaluation would require an extensive categorization of each lacuna's size using an image processing software to determine a more exact percentage for this parameter. This parameter directly influences the "Object Interpretation" parameter: the higher the Lacunas percentage of the model is, the less accurate is the interpretation that can be made of the model;
- **Other Physical Alterations:** Represent the macroscopic alterations that can be visualized in the model, such as glass fissures, paper tearing, adhesive bond strength loss, amongst others. While the "Lacunas" parameter could be incorporated in this analysis, it should be noted that the "Other Physical Alterations" parameter is assessing the stability of these alterations. For example, if an adhesive bond strength is unstable, meaning its condition is deteriorating, this may result in the separation of the paper/textile adhesive tapes from the glass edges, which may impact in the "Lacunas" parameter (in this case, if the adhesive tapes are lost, the "Lacunas" parameter would increase in value). This parameter should be evaluated on a scale of **1** to **5: 1** represents the **most unstable** conditions and **5** the **most stable** state;
- **Chemical Alterations:** Represents the macroscopic alterations that can be visualized in the model, and that one can associate with the commonly observed characteristics that are associated with chemical alterations of the different materials. For example: in glass, checking for the presence of crystals or iridescence; in paper, the existence of acid hydrolysis phenomena, resulting in the yellowing of the paper; in adhesives, the occurrence of cross-linking phenomena, which turns the adhesive yellow, causing it to lose its bond strength. This parameter should be evaluated according to the scale used in the "Other Physical Alterations" parameter. It is important to note that the chemical and physical alterations are always related, influencing each other;
- **Object Interpretation:** Represents the inference that can be extracted from the object's current condition, in respect to the model's original form. This parameter should be evaluated using a **Yes/No**

scale, depending on if it is possible or not to perceive the original form of the object. **Yes** – If it is possible; **No** – If it is not possible or if it is severely compromised.

Considering these parameters, each individual component should be evaluated, resulting in the average of all the attributed values, except for the "Lacunas" column where the attributed values should be summed to identify the total "Lacunas" in the model. Table 4 represent the resulting table applied to the example of model UL-DEP1308, presented in detail in Figure 6.

Table 4. Condition assessment example of the model UL-DEP1308

	Lacunas	Other Physical Alterations	Chemical Alterations	Object Interpretation
Labels	5%	3	2	Yes
Paper Tapes	15%	3	4	Yes
Glass	10%	4	5	Yes
Cardboard Model	5%	3	3	Yes
Inner Lines	-	-	-	-
Glass Crystal Model	**35%**	**3**	**3,5**	**Yes**
Object Condition		**Fair**		

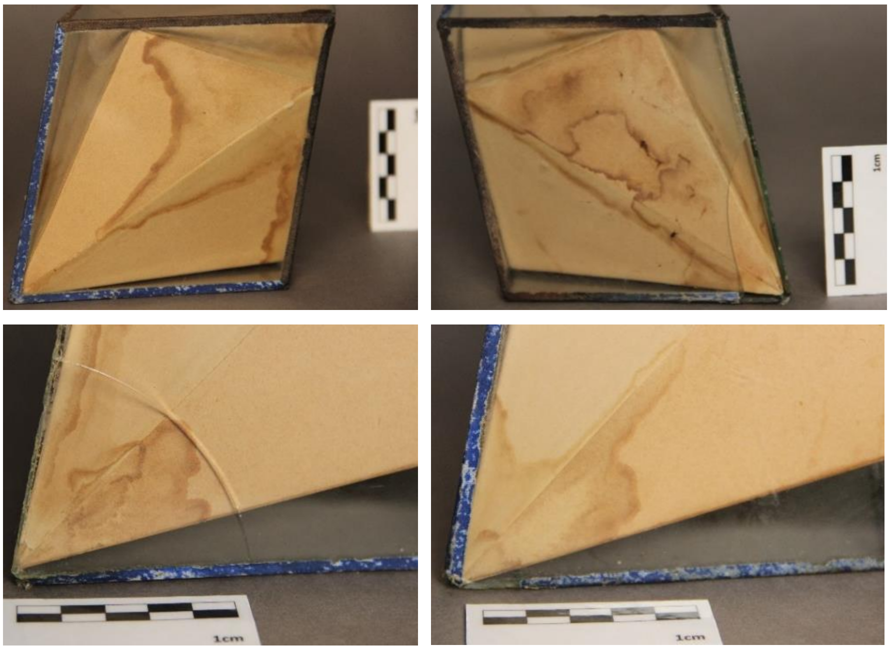


Figure 6. Details from model UL-DEP1308 from *Passos Manuel* high school collection currently in the MUHNAC. Pictures: MUHNAC, ®C. Peixe, February 2019

2.2. Analytic characterization – Analysis conditions[7]

The methodology hereby presented was already published by the research team in the article previously mentioned [13] (see Appendix I). Inner textile lines and paper/textile adhesive tapes were analysed by optical microscopy (OM). Different images were obtained with an Axioplan 2ie Zeiss microscope equipped with a transmitted and incident halogen light illuminator (tungsten light source, HAL 100); UV light (mercury light source, HBO 100 illuminator); and a digital Nikon camera DXM1200F, with Nikon ACT-1 application program software, for microphotographs. Samples were analysed with 10x ocular lenses and 5x/10x/20x/50x objective Epiplan lenses (giving total optical magnification of 50x, 100x, 200x, and 500x). Fibres were observed under OM, identified and categorized by morphologic characteristics [17]. The fibres samples were prepared with distilled water and separated from one another with the help of a needle under a magnifying lens and then mounted on the microscope slide for longitudinal view from lowest to higher magnification, under simple polarized light and cross polarized light. In total 33 samples of fibres were analysed, 6 of inner textile lines from 5 models of type A (Table 1), and 27 of paper/textile adhesive tapes from 15 models, on six different colours.

Microchemical tests were performed in samples of inner cardboard models (type B, Table 1) and to samples of paper labels. The Phloroglucinol Test was applied for lignin detection, using 1g of phloroglucinol dissolved in a mixture of 50ml methanol, 50 ml concentrated HCL and 50ml distilled water, according to TAPPI T401 norm [18]. The Aluminon Test was applied to check the presence of alumen salts, using a solution of 0.1g aluminon in 1l of distilled water [19]. The micro samples were placed on a glass rod and a small drop of each solution placed on different fibre sample where colour change was checked with the help of stereo binocular microscope. In the inner paper/cardboard models samples the Raspail Test was also tried for rosin detection, using an adapted methodology based on the TAPPI T408 norm [20]. First, a drop of saturated sugar solution (35g sucrose/20ml water) was applied into the sample placed on the glass rod, allowed to soak for one minute, and then the excess sugar solution was removed with filter paper. Follows the application of one drop of sulphuric acid (96.6% H_2SO_4) on sample and its observation with the help low power magnification. The reaction should be immediate, and the colour change may reveal the presence of alum rosin sizing [19].

Portable XRF was performed in situ, using Bruker S1 Titan Model 600, directly to the glass of 15 models, to determine the type of glass used to build the models. Three points were analysed for each model and the spectra were acquired under the following conditions: the excitation source is a Rh target X-ray tube of 4W, with maximum voltage of 50kV and 100µA, elemental range between Mg and U, and acquired with the integrated acquisition mode calibration GeoExploration, that operates at a 3-phase reading (90s totally): phase 1 at 30kV, 26 µA; phase 2 at 50kV, 26 µA; phase 3 at 15kV, 26 µA (30s each). Quantitative results were obtained with the automatic quantification proprietary software, Bruker Elemental S1. The elements initially not presented in oxides were then converted through oxide factors. To validate the obtained results, the glass standards from the CMoG B and D types were analysed under the same conditions [21].

Samples of adhesives on paper/textile adhesive tapes and on adhesives that join the glass surface were analysed by infrared spectroscopy in attenuated total reflectance mode (ATR-FTIR). The spectra were acquired using an Agilent Handheld 4300 FTIR Spectrometer with a DTGS detector, with controlled temperature, and a diamond ATR sample interface; the analyses were performed at the sample surface. All spectra were obtained with a resolution 8 cm^{-1} and 32 scans. In total, twenty adhesive samples were analysed.

From the categorization (Table 1 and 2), it was possible to select 15 models that may be considered representative of the collection. The first criteria was to select models from each typology presented in Table 1: 6 models from type A, 6 from type B, 1 from type C and, finally, 2 models from type D, ensuring access to all the materials that can be found in the models. The conservation state of the models was also considered: poor and fair condition models were preferred, since it is easier to collect samples and access to the interior materials in models that are less cohesive structurally. The selection comprehends, at least, 9 models attributed to the Krantz company, 5 altered models and 1 model that is proposed to be the only one that corresponds to the possible school-manufactured model (UL-DEP1249). All samples had a maximum size of a few millimetres and were collected from areas where the exterior glass was broken, areas that presented damage, (for example, ripped textile inner lines or detached paper/textile adhesive tapes) or samples where the adhesive was loose and accessible, and so, where the removal would not compromise the integrity of the object.

3. Results

3.1. Collection condition assessment

Through the condition scale presented in Chapter 2.1, it was possible to evaluate the 98 glass crystal models from the *Passos Manuel* high school, resulting in the collection's consolidated overall condition. These results are presented in Table 5, with examples of each state presented in Figure 7.

Table 5. Assessment of the *Passos Manuel* glass crystal model collection overall condition

Collection Condition State	Qt. (%)	Description	Needs
Good (Figure 7a)	28%	All components are in place and the models seem complete.	These models are physically and chemically stable; Regular care and monitoring.
Fair (Figure 7b)	49%	The components are partly fractured, teared, weakened or discoloured, but the models' integrity is not in total risk.	These models might need special storage or more frequent monitoring to better evaluate the materials' stability;
Poor (Figure 7c)	23%	Some components or parts may be missing and exists lack of adhesion between materials.	These models need an urgent treatment or special storage to avoid losing: part of a component and its correspondence to the model; losing any important information; or losing the whole object;

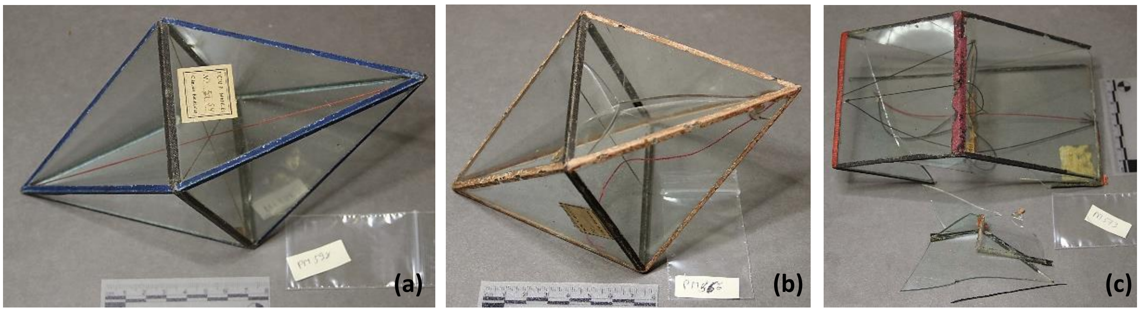


Figure 7. Examples of condition states from the *Passos Manuel* collection: **(a)** model in a good conservation condition, UL-DEP1295; **(b)** model in a fair conservation condition, UL-DEP1292; **(c)** model in a poor conservation condition, UL-DEP1323. Pictures: MUHNAC, ®C. Peixe, November 2018

Analysing the results presented in Table 5, it is important to emphasize that most of the collection's models are in a good or fair condition, representing 77% of the overall collection. An overall assessment in which only 23% (less than a quarter) of the models are considered in poor condition can be considered very positive for the collection's preservation, when considering that glass crystal model collections have, inherently, a very fragile nature due to the materials that constitute these models. Furthermore, when analysing the poor condition models in greater detail, it is also important to understand that the poor condition in the *Passos Manuel* collection could be substantial worse than the condition observed in the example of Figure 7c. This is evidenced by comparing the poor condition models of this collection with models of other scientific collections of similar contexts, such as the glass crystal model collection from the *Pedro Nunes* high school, presented in Figure 8.

Figure 8. *Pedro Nunes* high school glass crystal models collection: **(a)** example of the overall collection's storage conditions; **(b)** example of the bubble warp conditioning used in the models; **(c)** example of a poor condition model Picture: *Pedro Nunes* high school, ®C. Peixe, November 2018

The overall conditions in which the *Pedro Nunes* high school collection are stored, as exhibited in Figures 8a and 8b, can be considered deficient when compared to the monitoring and storage conditions that the *Passos Manuel* collection has available in the MUHNAC technical storage. This causes the models of the *Pedro Nunes* collection (mainly compose by Krantz company models) to be quite fractured, such as the example presented in Figure 8c. The poor condition of the example model is considerably worse than the poor condition model of the *Passos Manuel* collection presented in Figure 7c: despite both examples presenting fractured glass, the adhesives present in the model from figure 8c reacted differently to the bubble wrap conditioning, which lead to the adherence of the paper/textile adhesive tapes from the models to this bubble wrap packaging, deteriorating even further the model's already poor condition.

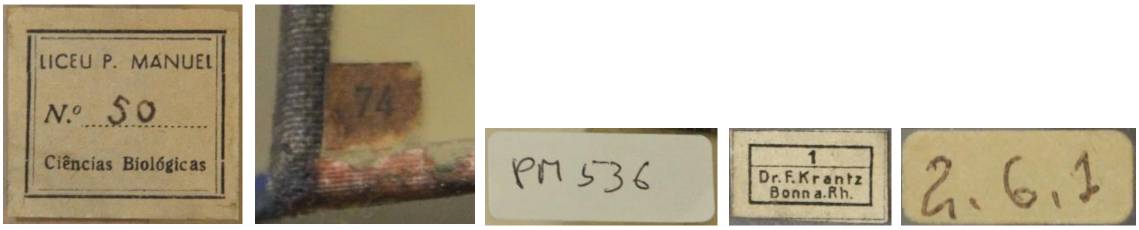
3.2. Analytical characterization results[7]

The analytical results obtained are presented by type of component, following the methodology as presented in Appendix I [13]. This allows to analyse all the information related to each component in a consolidated way, so that, all the different technical results performed in each component appear together, in order to better identify all the materials for each individual component. Doing so will enable to clarify, inside a component, which material is degrading the other or vice-versa, and understand if each material, per component, are original or post-fabrication repairs.

The presentation order is from the model's outside layer to the most inner one, to respect the order from the diagnosis procedure. From the 15 models that constitute the sample of the collection, there are five characteristic components identified and analysed, as follows: first, the paper/textile adhesive tapes and the adhesives form the joining edges analysed by OM and ATR-FTIR; then, the paper labels and the respective adhesives analysed by MT and ATR-FTIR; next, the glass characterization using p-XRF; the inner paper/cardboard models using MT; and finally, the inner textile lines using OM.

3.2.1. Paper labels

The different types of paper labels present in the glass crystal models from the *Passos Manuel* high school collection are presented in Figure 9.



(a) **(b)** **(c)** **(d)** **(e)**

Figure 9. Glass crystal models labels: **(a)** Liceu P. Manuel; **(b)** Smaller labels with no given correspondence; **(c)** Register; **(d)** Krantz Company; **(e)** Other labels. Pictures: MUHNAC, ®C. Peixe, February 2019

The labels identified are as follows: the label from *Passos Manuel* high school ("Liceu P. Manuel"), shown in Figure 9a, which makes the correspondence with a list of the names from the different crystal representations; smaller labels (Figure 9b), whose correspondence is undetermined; current register labels (Figure 9c), a number attributed at *Passos Manuel* high school to each model from the collection enter the museum. Apart from these three main labels, that appear in most of the models, there are labels from the Krantz company (Figure 9d) present in 4 different models, and a few other different types of labels (Figure 9e) present in 15 models, such as labels with names or numbers, with no matching correspondence determined. From the labels described, the only one that was not considered historic is the current register label; the time they were attached to the models does not correspond to their historic use.

Over time, labels become an historic part of the objects, with irreplaceable information about them, and so their preservation is as important as any other component [22]. Register labels were not analysed, since they are temporary labels. Paper labels characterization results were divided by the 2 main materials that constitute them: small paper samples, in order to identify lignin and alumen salts to acknowledge the quality of this paper; and adhesive, to recognize which type were used. The Raspail test, to identify rosin, were not performed in the labels since the amount of sample available was insufficient to adequately conduct this analysis.

Paper samples

Microchemical tests of phloroglucinol and aluminon were performed for all labels deemed as historic and the results are presented in Table 6 and Table 7, respectively.

Table 6. Phloroglucinol spot test on different paper labels

Accession no.	*Liceu P. Manuel*	Smaller labels	Krantz	Other labels
UL-DEP1240	-	-	-	Negative
UL-DEP1249	-	-	-	Positive
UL-DEP1252	Negative	Positive	-	-
UL-DEP1287	-	-	-	Negative
UL-DEP1293	Negative	Positive	-	-
UL-DEP1308	Negative	Positive	-	-
UL-DEP1309	-	-	Negative	-
UL-DEP1321	Negative	-	-	-

Table 7. Aluminon test on different paper labels

Accession no.	*Liceu P. Manuel*	Smaller labels	Krantz	Other labels
UL-DEP1240	-	-	-	Negative
UL-DEP1249	-	-	-	Positive
UL-DEP1252	Positive	Negative	-	-
UL-DEP1287	-	-	-	Positive
UL-DEP1293	Positive	Negative	-	-
UL-DEP1308	Positive	Negative	-	-
UL-DEP1309	-	-	Negative	-
UL-DEP1321	Positive	-	-	-

Results are consistent for each type of labels, apart from the category ‘other labels’ that reveal some inconsistent results. It is important to note the reduced number of existing Krantz company labels (as mentioned in Chapter 1.2.1, there were only 4 Krantz labels present in the models, suspected to belong to the same generation, since they presented similar macroscopic characteristics, corresponding to models present in the same Krantz company catalogue [14]); a decision was made, in order to maintain the current condition of these labels, that only one representative sample would be collected. Considering this limitation, the inferences made in respect to the Krantz labels should be taken into consideration with caution.

Analysing each type of label separately, the paper with the highest quality is the one from Krantz Company, due to the absence of lignin (phloroglucinol test) and alumen (aluminon test). The *Liceu P. Manuel* labels also present good quality, based in the absence of lignin, despite the presence of alumen salts; the latter may cause acid hydrolysis of paper, and so, represents a warning to the label's deterioration. The smaller labels do not reveal alumen salts, but the presence of lignin was detected, which is a sign of mechanical wood pulp production and, therefore, acid hydrolysis deterioration can worsen at any time. Finally, the 'other labels' did not present constant results, alternating between good and bad quality.

Adhesive

By means of ATR-FTIR the adhesive present in the labels was also analysed and the obtained spectrum is presented in Figure 10.

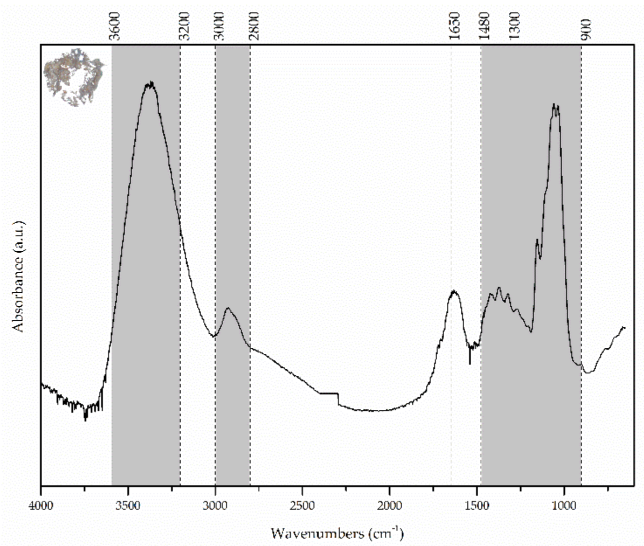


Figure 10. ATR-FTIR spectrum of gum Arabic from sample of UL-DEP1308

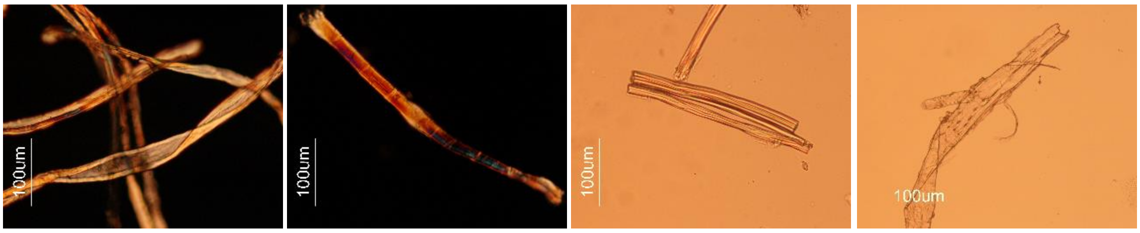
In the spectrum presented in Figure 10, the presence of gum Arabic was identified. This material is characterized by one peak at ca. 1650 cm^{-1} of the O-H bending band and four typical regions, from O-H stretching band between ca. 3600-3200 cm^{-1}, C-H stretching band between ca. 3000-2800 cm^{-1}, C-H bending band between ca. 1480-1300 cm^{-1} and finally C-O stretching bands between 1300-900 cm^{-1} [23]. In this spectrum all bands characteristic of gum Arabic can be observed.

3.2.2. Paper/textile adhesive tapes and edges adhesives

Paper/textile adhesive tapes characterization results were also divided by its 2 main materials, paper/textile fibres, in order to try to identify them, and adhesive, to recognize which type were used originally and which ones are repairs, since different samples from adhesive were collected due to appear differently at naked eye.

Paper/textile fibres

Observing the paper/textile adhesive tapes fibres, it is in fact possible to identify different types of fibres, such as textile fibres (also commonly observed in manual paper) and wood paper fibres, the expected ones to be found in industrial paper, as mentioned before. The paper/textile adhesive tapes found in the selected models to analyse are constituted by one or more different types of fibres. The observation was made under the OM and the obtained images are presented in Figure 11.



(a) **(b)** **(c)** **(d)**

Figure 11. Fibres under optical microscope: **(a)** cotton **s**ample example from UL-DEP1287 model; **(b)** flax or hemp sample from UL-DEP1312 model; **(c)** jute sample from UL-DEP1268 model; **(d)** softwood sample from UL-DEP1234 model

Obtained OM images were compared with the literature from the Conservation and Art Materials Encyclopedia (CAMEO) database [24]. The results are a mixture of fibres, with cotton being the most common. These fibres can be identified by their typical characteristics: flat fibres revealing ribbon-like twisted areas as cotton (Figure 11a); lines going across the fibre and forming cross-hatching and knots as flax or hemp (Figure 10b); and longitudinal lines for jute fibres (Figure 11c). The presence of softwood (Figure 11d) was still possible to observe, with its characteristic sequenced pits and other species' features, such as ray parenchyma. Nevertheless, it is worth to mention that this last fibre was only identified in a specific model, UL-DEP1234, which shows a substantially different black tape, when compared with other black tapes from other models, possibly applied during repairing.

Adhesive

The adhesives from the paper/textile tapes and from the joining glass edges were analysed by ATR-FTIR, under the conditions described in Chapter 2.2, in order to identify its molecular characterization. From the 17 adhesive samples with the characteristics above analysed by ATR-FTIR, 7 were identified as only protein glue, 4 as protein glue and cellulose, 1 as only cellulose, and in 5 of the samples other components were identified. Three of the last five samples contained protein, cellulose and materials that were identified as gypsum, kaolin and shellac, and in 2 of them the presence of PVAc was also identified. The presence of these materials is, possibly, due to the result of some changes made by the school professors, or other professionals, during the period of use of the models, with the possible objective of making the necessary repairs for the models to become useful and usable again, as referred in chapter 1.1.3 by a personal communication [9].

Spectra from three samples that were collected from different parts of the models, being UL-DEP1308 (a) from an edge of glass without paper adhesive tape, UL-DEP1308 (b) from a glass face near a paper adhesive tape and UL-DEP1309 (c) from an edge of glass that had not been in contact with paper adhesive tape, are presented in Figure 12.

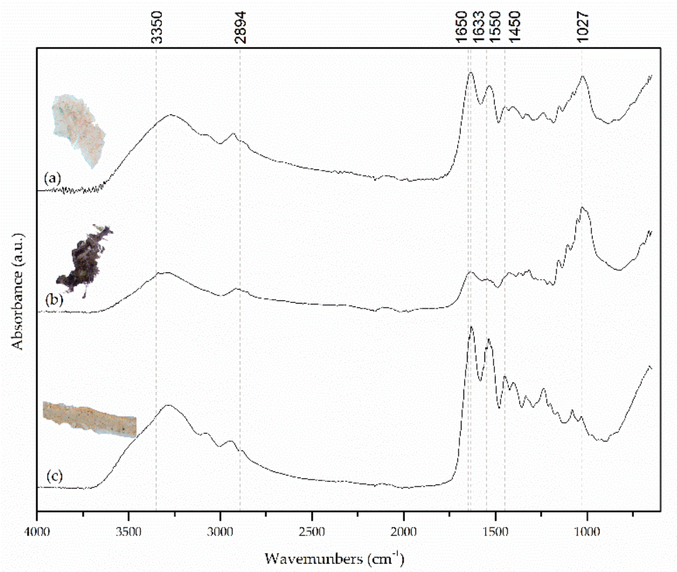


Figure 12. ATR-FTIR spectra of **(a)** protein and cellulose and **(b)** cellulose samples from UL-DEP1308 model and **(c)** protein sample from UL-DEP1309 models.

Two types of materials were identified, protein (b) and cellulose (c), with (a) being a composite material constituted by a mixture of protein and cellulose. Protein spectra are typically recognized by the presence of the carbonyl group belonging to the amide I (ca. 1650 cm^{-1}) and of amide II (ca. 1550 cm^{-1}). These, along with a third one, usually named by amide III (ca. 1450 cm^{-1}), form the characteristic stair-step pattern. When coupled with the N-H stretching band (centred at 3350 cm^{-1}), it is possible to confirm the presence of the amide, and so, the protein [23]. Therefore, it is possible to infer that one of the adhesives present must be some type of protein glue (samples (a) and (b)), such as it presents bands at ca. 1630 cm^{-1}, ca. 1536 cm^{-1} and ca. 1454 cm^{-1} amide I II and III, respectively, and at ca. 3275 cm^{-1} the N-H stretching band, despite being impossible to further determine which one.

Cellulose spectra can be recognized by two regions of absorbing bands, first between ca. 3660-2800 cm^{-1} and second ca. 1650-400 cm^{-1}. The first region is characterized by the stretching vibration of the hydroxyl group (centred at ca. 3331 cm^{-1}) and the band attributed to CH stretching vibration of the hydrocarbon groups in polysaccharides (ca. 2894 cm^{-1}). The second region comprises the band vibration of water (ca. 1633 cm^{-1}) and stretching and bending vibrations of $-CH_2$ and -CH, -OH and C-O bonds of cellulose (at ca. 1428, 1367, 1334, 1027 and 896 cm^{-1}) [25]. It is possible to say that the analysed sample contain cellulose, with the stretching vibration of the hydroxyl group appearing at ca. 3290 cm^{-1} and the CH stretching vibration of the hydrocarbon groups at ca. 2915 cm^{-1}, and then some stretching and bending vibrations of $-CH_2$ and -CH, -OH and C-O at ca. 1637 cm^{-1} and ca. 1027 cm^{-1}. The presence of cellulose can be proved since the characteristic bands can be observed.

Apart from this, different types of materials were identified, and the corresponding spectra are presented in Figure 13.

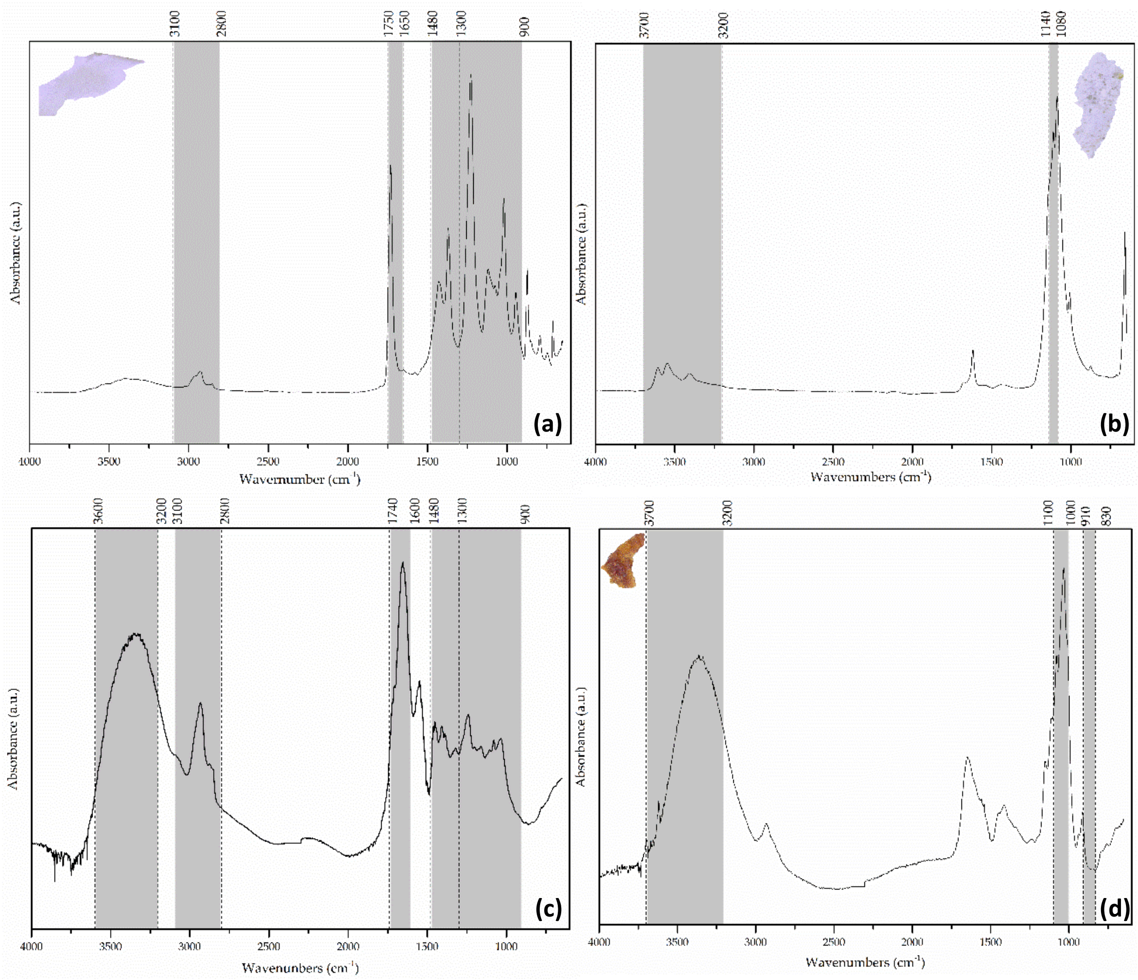


Figure 13. ATR-FTIR spectrum of **(a)** PVAc from sample of UL-DEP1287 model; **(b)** gypsum from sample of UL-DEP1316 model; **(b)** shellac from sample of UL-DEP1269; **(c)** kaolin from sample of UL-DEP1316

The ATR-FTIR results of these materials (Figure 13) shown their characteristic bands. PVAc (Figure 13a) is generally identified by bands at four different regions, C-H stretching bands at ca. 3100-2800 cm^{-1}, C=O stretching band at ca. 1750-1650 cm^{-1}, C-H bending bands at ca. 1480-1300 cm^{-1} and C-O stretching bands at ca. 1300-900 cm^{-1} [17]. Gypsum (Figure 13b) is normally identified by an asymmetric SO_4^{3-} stretching band between ca. 1140-1080 cm^{-1} and an antisymmetric and symmetric O-H stretching bands [23]. Shellac (Figure 13c) have their typical bands at five different regions, the O-H stretching band at ca. 3600-3200 cm^{-1}, the C-H stretching bands at ca. 3100-2800 cm^{-1}, the C=O stretching band at ca. 1740-1640 cm^{-1}, the C-H bending bands at ca. 1480-1300 cm^{-1} and the C-O stretching bands at ca. 1300-900 cm^{-1} [23]. Finally, kaolin (Figure 13d) is normally identified by three different regions, the O-H stretching bands at ca. 3700-3200 cm^{-1}, the asymmetric Si-O-Si stretching bands at ca. 1100-1000 cm^{-1} and Si-O stretching bands at ca. 910-830 cm^{-1} [23].

The PVAc adhesive, from the 15 models selected to collect samples, were also present in another model, this one coloured black, possibly to match the colour from the tape where it would be applied. The identification of these 4 materials (PVAc, gypsum, shellac and kaolin) strengthens the hypothesis that the models suffered alterations and repairs that become necessary with time and use, also proved in chapter 1.1.3 by personal communication [9]. Since PVAc is an adhesive from the 20th century, this is probably not originally part of glass crystal models, since PVAc appeared later than glass crystal models from Krantz company, from where *Passos Manuel* high school collection is believed to be originated from.

3.2.3.Glass characterization

To determine the glass chemical composition, a p-XRF equipment was used, with the conditions described in Chapter 2.2. Three measurements were performed for each model. The results listed in Table 9 in Appendix II are an arithmetic average of the values obtained from the three measurements, with the respective value for the standard deviation. In order to identify the type of glass used to build glass crystal models the contents of calcium oxide (CaO) and potassium oxide (K_2O) were related and compared to the standards from Corning Museum of Glass (CMoG) B and D; said comparison is presented in Figure 14.

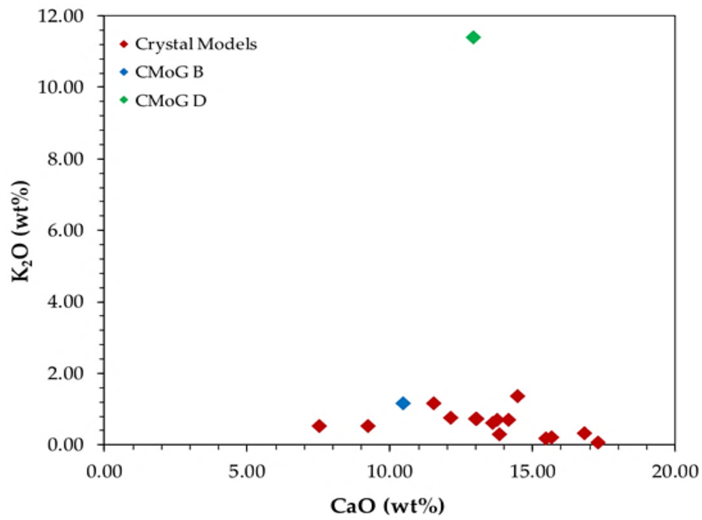


Figure 14. Binary plot of calcium oxide vs. potassium oxide, in weight percent of oxides and measured by p-XRF.

It is possible to infer that the glasses from the *Passos Manuel* high school glass crystal models are of soda rich type, once these are grouped in the same area of the chart that the CMoG B standard (sodium rich standard).

The p-XRF technique used to characterize the glasses does not allow to determine the sodium oxide content; since it is a light element, usually it needs an in vacuum setup to be determined. The content of potassium oxide is, in most models, below 1 wt%, which prevents the glass from being considered of a potassium rich composition or a mixed alkali composition [26]. Moreover, the contents of lead are all below 0.1 wt%, preventing the glass from being of a lead rich type (lead contents above 25 wt%), supporting the proposed glass type.

3.2.4. Inner paper/cardboard models

Regarding the inner paper/cardboards models microchemical testing, the results can be observed in Table 8.

Table 8. Microchemical tests on models with inner paper/cardboard models.

Accession No.	Phloroglucinol Test	Aluminon Test	Raspail Test
UL-DEP1249	Positive	Positive	Positive
UL-DEP1252	Negative	Positive	Positive
UL-DEP1287	Negative	Positive	Positive
UL-DEP1308	Negative	Positive	Positive

Phloroglucinol spot test was negative except in one case (UL-DEP1249). This means that only in this case it was found the presence of lignin. The Aluminon test for alumen salts detection and Raspail test for alum rosin are both positive for all cardboard models. So, when coupling this information with the characterization performed in detail in Chapter 1.2.1, one can conclude that the model UL-DEP1249, that corresponds to the proposed school-manufactured model, was manufactured using very poor materials, while the remaining models were produced using lignin free cardboards, despite revealing also an acid source, due to the presence of rosin as sizing material.

3.2.5. Inner textile lines

Through the observation of the inner textile line fibres it was possible to notice that these are not a single type of fibre but mixtures, as shown in Figure 15.

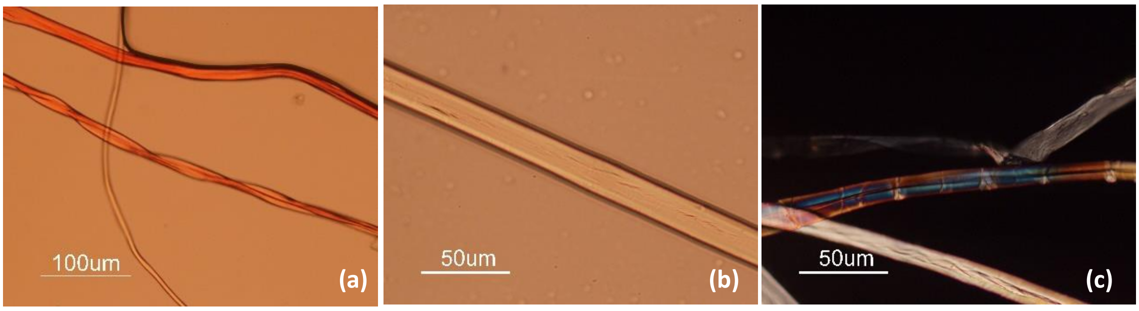


Figure 15. Fibres under optical microscope: **(a)** red inner textile line from UL-DEP1316 model (cotton); **(b)** beige inner textile line from UL-DEP1312 model (cultivated silk); (c) beige inner textile line from UL-DEP1268 model (flax or hemp).

The observation under the OM (Figure 15) and the comparison with the CAMEO database and the bibliography [18] [21] suggests the presence of cotton, a flat fibre revealing ribbon-like twisted appearance areas, thick walls and a small lumen under the microscope (Figure 15a), cultivated silk with a smooth appearance and lustrous filaments (Figure 15b) and even traces of flax or hemp with the presence of lines going across the fibre and forming cross-hatching and knots, plus a narrow lumen (Figure 15c).

3.3. Discussion[7]

The results obtained through analytical characterization of the different components that constitute the glass crystal models from *Passos Manuel* collection allowed identifying several types of materials present in the components. This was the main objective of the analytical characterization proposed, which revealed that the different components of the models are produced from three major materials: glass, paper and adhesives. It is important to further analyse the results obtained, to estimate with more precision the production era of the models and, consequently, understand the process by which its materials were made and used. Finally, it is necessary to discuss if said materials are in a stable conservation state or not. By doing so, it is also possible to establish a more informed background of the materials in the models and define a better diagnostic for the glass crystal models collection.

3.3.1. Glass

By observing through naked eye, it is possible to conclude that the glass sheets that compose the glass crystal models in study do not present bubbles or any signs that this material was produced using any blowing technique. Relating this with the fact that these models possibly belong to the Krantz company chronology, it is possible to propose the use of float glass to build these models. Float glass, also known as window glass, is and industrial process of glass sheets production. More detailed information about this process is presented in Appendix III. When coupling this with the composition proposed, in Chapter 3.2.3 (glass of a soda rich type), it is possible to infer that this type glass has low susceptibility to degradation, being a stable composition. The calcium oxide content, observed in all the 15 models analysed, was estimated as above 10 wt% which acts as a matrix stabilizer (property modifier), contributing to the resistance that this type of glass has to degradation [27]. None of the 98 models from the *Passos Manuel* high school collection presented crystals or iridescent areas were observed on glass sheets.

3.3.2. Paper

Considering now the papers and cardboards, comparing the obtained results with the Krantz company chronology, it is possible to propose that they belong to the first full industrial era of paper production. In this era, detrimental materials, such as lignin and rosin, were expected to be found. One of the first studies, developed in Germany, on the deterioration of paper followed the creation of the first laboratories for paper testing in 1884 [28]. There, the presence of lignin was classified as one of the main intrinsic causes of the deterioration of industrial paper. Later, around 1920, Switzerland researchers identified the presence of acidic salts of alumen in paper as an additional contributing factor for paper deterioration [28] [29]. The referred substances act as catalysts for acid hydrolysis, which is one of the main degradation problems from cellulose, which, consequently, will contribute to the breakdown of the polymer chain, affecting the glycosidic bonds that link the glucose units of the cellulose [28]. Acids will be formed and catalyse the hydrolysis, initiating a continuous process of cellulose degradation [30] [31]. In fact, the described phenomenon affects even better-quality paper, which will contribute to the ageing and deterioration of cellulose, depending on the influence of external factors such as environmental conditions and storage [28]. Despite this, the main results, for paper and cardboard, revealed the choice of reasonable quality papers for the model's production, proven by the absence of lignin. Even so, the presence of alumen salts possible from a rosin sizing, especially in the cardboard models is a real concern, increasing the risk of deterioration by acid hydrolysis and its collapse over time inside the glass crystal model [13].

Considering the paper labels results from the *Passos Manuel* high school label and the ones from Krantz company, tests revealed that these components are from fair and good quality, due to the absence of lignin as referred above. On the other hand, small labels are composed by very poor materials which can result in its rapid degradation and, consequently, loss. In respect to the 'other labels', some with poor quality (presence of lignin and alumen salts), their preservation is important, since in the future these labels may solve historians' doubts about relevant information of the models (since they have numbers and names records). To do so, their degradation process due to the presence of alumen salts can be corrected if some neutralizing conservation is applied to them.

3.3.3. Adhesives

Looking to the adhesive results obtained, the ones collected from the paper/textile adhesive tape proved to be major of a protein nature. In terms of conservation, protein adhesives can suffer biodeterioration attacks and, depending on the adhesive, these can lose their integrity and adhesive power with age and under certain conditions such as very high or very low relative humidity and temperature. Some tapes are already detaching from the glass, which can be a sign that the adhesives are not entirely fulfilling their function. As it was possible to evaluate, no signs of biodeterioration was identified. However, the need of short period monitoring is clear, since the protein adhesives may lose their remaining adhesive power, which will result in the collapse of the entire system of the model. In terms of the other characterized materials (PVAc, gypsum, shellac and kaolin), these were identified as repairs. Nevertheless, they are part of the model's history and should be treated as an integral part of the model.

4. Conclusion

The present work aimed to achieve two main goals: perform an accurate assessment of the *Passos Manuel* high school glass crystal models collection condition and obtain the analytical composition of the 98 models that constitute this scientific collection. This is a preliminary study that precedes the development of a conservation and restoration methodology for glass crystal models and serves as a baseline in which the full characterization of the collection may be achieved. Such methodology should contemplate appropriate guidelines to perform in situ preservation, similarly to the objective of the research initiatives promoted by MUHNAC with several institutions that own this type of scientific heritage.

As a first approach, it was necessary to perform a macroscopic overview of the 98 glass crystal models to establish a first characterization based on the model's main observable characteristics. Realizing that the main components of the resulting typologies' categorization (Table 1) presented some differences, the need to perform a comparison with different catalogues seemed necessary. One of the main conclusions to be drawn of this second categorization is the identification of the provenance of most of the collection – when comparing the *Passos Manuel* high school models to the Krantz company catalogues, it was possible to ensure the provenance of 85 models. This yielded important information to bear in mind when analysing the remaining results obtained from the ensuing methodologies that would be conducted.

The assessment of the conservation state of the collection was also crucial to establish the starting point of the preservation of the overall collection, from which a proper conservation and restoration methodology should be developed, while simultaneously identifying the main problems affecting this type of collections. The collection of glass crystal models from *Passos Manuel* high school was assessed recurring to a custom condition scale, developed to better suit the reality of this type of collection. Overall, the collection's condition is positive (at least 77% of the models were in a fair or good condition), which is remarkable when considering the fragility of this type of collection. Nevertheless, without proper care or preservation guidelines and awareness provided to the owner institutions the condition of glass crystal models collections can rapidly deteriorate (as evidenced by the comparison of the *Passos Manuel* high school collection with the one from *Pedro Nunes* high school), ultimately resulting in their disappearance.

To determine the different materials that constituted the different components and better distinguish the original material from the repairs, several characterization techniques were performed in each component. Paper/textile adhesive tapes, analysed by OM and ATR-FTIR, have in its compositions paper and textile fibres (cotton, flax or hemp and jute), and the original adhesive is suggested to be a type of protein glue. Nevertheless, four more materials were found (gypsum, kaolin, shellac and PVAc) present in these components, possibly due to scholar context repairs. The paper labels, analysed by MT and ATR-FTIR, seem to be constituted by paper from good quality, without lignin and alumen. The 'other labels' altered between good and bad quality. The adhesive present in these was identified as gum Arabic. The glass sheets, analysed by p-XRF, are suggested to be of soda rich type glass, possibly float glass. This is also evidenced when analysing the results from the comparison established with the CMoG B standards in Figure 14. Concerning the inner paper/cardboard models, they were analysed by MT and, apart from the school-manufactured model that is of poor quality (with presence of lignin, alumen and rosin), all the others are of good quality. Finally, the inner textile lines, analysed by OM, revealed to be made from cotton, cultivated silk and flax or hemp.

Through this characterization's methodology, it was possible to distinguish models' original materials from repairs. This is noticed, for example, in the analysis preformed for the paper/textile adhesive tapes. OM observation revealed the presence of softwood paper fibres in the UL-DEP1234 black tape; these fibres were not identified in the other samples observed, being this an example of repairs identification with the methodology conducted. Therefore, it is possible to suggest that the examination and analysis methods applied to characterize this glass crystal models collection can be reproduced in other situations, whether for the validation of original materials, or to check the materials used for repairs. Since the selected methods were considered for being portable and adjustable, this methodology also allows to analyse a large diversity of forms, objects and materials.

This work represents a baseline that can be considered and consulted when developing a conservation and restoration methodology for the *Passos Manuel* glass crystal model collection. It identifies the main materials present in the models and presents a global overview of the collection condition and major problems that affect its preservation. It also provided valuable insight on a first approach that is proposed to be followed when analysing these types of scientific collections, to establish a starting point from which conservators may develop procedures to assure the preservation of glass crystal models.

Further work may be developed to complete the study. Regarding the metal nuts and screws, it is suggested that its characterization should be performed, to understand which metals are present and if it is deteriorating itself or the other materials present in the glass crystal models. This work represents an initial approach to develop a conservation and restoration methodology for glass crystal model collections. Based on the resulting characterization of the collection, an in-depth methodology can be thoroughly developed, using the information of the present work as an important baseline.

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Appendix I – “Glass Crystal Models: A First Approah to a Hidden Treasure of Teaching and Scientific Heritage”

heritage

MDPI

Communication

Glass Crystal Models: A First Approach to a Hidden Treasure of Teaching and Scientific Heritage

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Abstract: Glass crystal models arrived in Portugal around the late 19th century, when high schools, universities, and polytechnics were gradually provided with teaching collections to support science education. Therefore, they are an important material evidence of teaching methodologies of mineral and geology science in the 20th century. The Passos Manuel high school in Lisbon, owns a significant collection of scientific heritage, currently on a long-term loan at the National Museum of Natural History and Science and the University of Lisbon, which includes a set of 98 glass crystal models. Besides glass, these models are composed by adhesives, paper, cardboard, textile threads, paper/textile adhesive tapes, and metal nuts and screws. Also, they show several levels of intervention and different conservation states. In this paper, the first results of a multi-analytic approach to chemically characterize these objects' material composition will be presented. Characterization was done based on portable equipment (pXRF), or by collecting small samples further analyzed using optical microscopy and FTIR-ATR techniques. This study allowed for a first distinction between original materials from the old repairs; to develop a more accurate assessment of the conservation condition; and finally, as one of the main aims of this work, to determine preventive conservation measures in order to better preserve these cultural objects.

Keywords: glass crystal models; teaching collections; material characterization; preventive conservation; scientific heritage

1. Introduction

1.1. Historic Background: Comprehending the Origins of Glass Crystal Models

Late in the 16th century, the study of crystals was mostly done through books on minerals and mining industries [1]. In 1546, the first book on mineralogy, *De Natura Fossilium* by Georgius Agricola (1494–1555), was edited. In this book, the classification of minerals was divided by their physical characteristics, that is, color, weight, transparency, shine, flavor, smell, shape, and texture [1,2]. *De Natura Fossilium* came to demystify the superpowers of minerals, presenting them for their natural properties and also stressing out the importance of the different geometric forms [1].

Throughout the 16th century, several studies on mineralogy were published, among them *De Subtilitate* (1550) by the Italian Girolamo Cardano (1501–1576); *De Re Metallica* (1551) by Christoph Entzelt (1517–1586); and in the year of 1556, Georgius Agricola launched his work, also entitled *De Re Metallica*, that mainly approached mining techniques, but he also related the minerals by their physical characteristics and mentioned the variety of crystalline forms of the minerals [1].

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It is worth mentioning the work of Wentzel Jamitzer (1508–1586), a master goldsmith and German jeweller, who published the results of his study, *Perspectiva Corporum Regularium*, in 1568, which consisted of preparing 140 models with geometric shapes. After that, in 1621, Willebrord Snel (1580–1626) discovered the law of the refraction of light when it crosses a liquid. This would be a discovery of great importance for crystallography, however, it was only revealed through a mention in the book of Vossius, *De Lucis Natura et Proprietate* (1662) [1]. So, as early as 1665, Robert Hook (1635–1703) published *Micrographia*, where he described and observed under the microscope countless materials including some crystals. Hook described the regularity of the angles between corresponding faces, regardless of the infinite variety of crystal sizes [1].

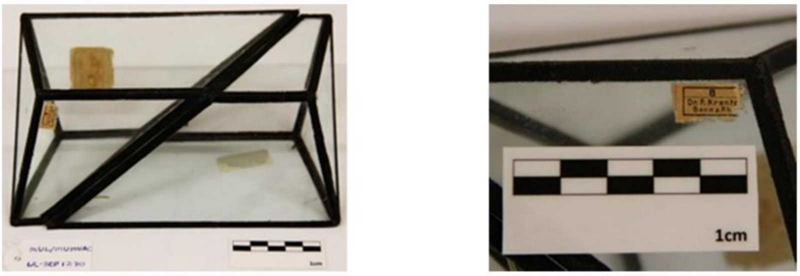
Despite the developments of the 16th and 17th centuries, the first known references to crystallographic models linked to mineralogy only appear in the 18th century. After 1735, the Swedish naturalist C. Linneaus (1707–1778) prepared these types of models in wood. However, it was only in the 1780s that crystallographic models were connected to crystallography studies. These were created as a way to give a 3D vision, as until then the models were only seen as flat drawings [3]. In 1772, Romé de L'Isle (1736–1790) published the first edition of the famous *Essai de Cristallographie*, where crystallography and mineralogy were defined as science. This book included illustrations, which the author called developments, that consisted of foldable surfaces that contained lines enabling a 3D reconstruction of the shape of the crystals [3]. After the success of the first edition, the author then released a second one, more extensive, with 483 illustrations of crystals and minerals from his private collection. With the support of a recorder and two students, 3D terracotta models were created to be sent to their subscribers as a prize [3].

After the development of the goniometer prototype by Carageot in 1780, it became possible to measure interplanar angles close to half a degree, which was viable due to the use of terracotta models instead of natural crystals [3]. After approximately 20 years, terracotta was replaced by wood (Figure 1), since it allowed for softer faces, more defined edges, and a greater rigor in the creation of angles [3]. Since the introduction of these models by Romé L'Isle, the quantity of its production increased, being simultaneously required as models for education and for mineral collections [3].

(**a**) (**b**)

Figure 1. Crystal models in 3D made of wood. (**a**) Box with a set of wooden crystal models and (**b**) wood crystal model from a box set (UL-DEP1325), both from the Passos Manuel high school collection, currently at MUHNAC.

Throughout the 19th century, the importance of these collections in science education at university level, as well as in secondary and primary education, led to the emergence of a global industry with a focus on France, Germany, and England. The creation of the Krantz company at Bonn in 1833, fit the increasing production and requisition of these materials. The company was set by the hand of Adam August Krantz, who started the production of crystallographic models in glass (Figure 2) [4]. The company still runs under the rule of the same family [4].



(a) (b)

Figure 2. Glass crystal model (UL-DEP1270) from the Passos Manuel high school collection at MUHNAC (**a**) model with label from Krantz Company; (**b**) detail of the label from Krantz company.

1.2. Passos Manuel High School and the Models under Study

Glass crystal models collection, the case study treated in this paper, is nowadays part of the natural history teaching collection of an important and centenary Portuguese high school, the Passos Manuel, which was founded following the education law of November 17 of 1836 by the minister Manuel da Silva Passos (1805–1862), also known as Passos Manuel [5]. This law established the high schools' network across the country districts under the national plan for the improvement of secondary education (following the French 'lycée' as a model) [6]. The full study of these collections enables a better comprehension of past teaching methodologies and as well, unveils aims, policies, and practices of science teaching in Portugal during the mid-nineteenth and twentieth centuries. Furthermore, it also contributes to add value to these collections as a historical material evidence of scientific heritage, and ultimately, to the development of good practices for their long-term preservation.

From the perspective of the history of science, the study of this particular set of glass models underlines the relevance of material cultures as primary sources through their interpretation, fostering the knowledge about their use in teaching practices, along with the collection's connection with the education policies on the reorganization of science teaching in Portugal, which, at the time, appears to have been transversal to whole country [6]. Also, the objects' biography promotes the understanding of their significance within a particular school community and their importance in the knowledge transfer process in a certain space and time.

On the other hand, from the perspective of material and conservation science, the full study of glass crystal models will enable researchers and conservators to increase knowledge about manufacturing methods, deterioration processes, and preservation needs. The compositional characterization of their materials will strongly contribute to the development of conservation and restoration methodologies, along with preventive conservation guidelines that will ultimately provide schools, museums, and other institutions with tools to better preserve their glass crystal models. Besides raising the awareness about this important legacy, this last perspective is thus the main aim of this paper besides. In fact, as far as the authors know, this is the first systematic study that focuses on the glass crystal models collection, with the aim of performing an accurate assessment of its conservation condition and determining preventive conservation measures in order to better preserve the models for the present and future generations.

The crystal glass models under study are in storage and long-term deposit at Museu Nacional de História Natural e da Ciência (MUNHAC), but as previously mentioned they belonged to Passos Manuel high school. This school possesses a vast collection of scientific instruments and specimens of natural history (such as chemicals glass containers, fluid, and taxidermized specimen collections, among others), as well as crystallographic models, namely wood models present in large quantities and 98 crystal glass models. The latter are fragile three-dimensional composite items with a certain complexity. They are mainly formed by glass surfaces and large quantities of paper, present in the geometric figures kept inside the glass surfaces, in the paper adhesive tapes to join the glass edges, and in several paper labels with manuscript ink, used in different inventories. Some of the glass crystal models also show threads and metal nuts and screws. MUHNAC have the responsibility to preserve and to promote the access to this collection, in general in a fair condition but, until now, these have been little studied. Also, considering some of the visible conservation problems and the need for safe long-term loan and availability of the collection, its further study represents a great challenge. Thus arose the possibility to set a project for the interdisciplinary study of these glass crystal models, under the partnership between MUHNAC, VICARTE (research unit 'Vidro e Cerâmica para as Artes', in English 'Glass and Ceramics for the Arts', NOVA School of Science and Technology (FCT NOVA)) and the Conservation and Restoration Department, FCT NOVA. Preliminary working methodology involved a macro observation and systematization of the entire set by form and/or main materials through visual identification. In Portugal, the provision of high schools with natural history collections to support science teaching was considered a priority for the Portuguese government, namely after Passos Manuel reform. In 1895, the discipline of natural history was integrated into the curriculum of secondary education and despite some criticisms regarding the lack of material, it is known that at that time more than 70% of high schools had collections of zoological, botanical, geological, and mineralogical specimens [6]. It is believed that the increasing of availability of this type of model happened in the 20th century. This is the case of Passos Manuel high school, from where one can find a large number of crystal wooden models (Figure 1b) and 98 glass crystal models, some of these still with labels from the Krantz company (Figure 2a,b).

In the absence of any reference to a national manufacturer of such models, it is highly probable that most of the glass crystal models would have been imported from abroad. They were then distributed to the country's main high schools when science disciplines were also established in the education curriculum. According to a survey made in historic record sources dated to between 1966 and 1972, many requisitions of crystallographic models of wood and plastic were made. This is probably linked to the fact that the fragility of glass made it easier to request models of other materials [6]. In relation to glass crystal models, these are also found in large numbers in schools, namely high schools, polytechnics, and universities in Portugal, with more found in the main cities [6].

The importance of this study is also related to the experimental designed used, since it operated nondestructively to quasi-destructive and aimed at: (i) Distinguishing the original materials from latter repairs/alterations; (ii) performing an accurate assessment of the conservation conditions and preservation needs of these objects; and, (iii) determining preventive conservation measures, in order to better preserve these cultural and scientific objects. The main results, still from a preliminary approach, will be presented in this paper.

2. Analytic Study: Materials and Methods

The preliminary approach to the study of the glass crystal models collection involved macro observation that allowed for the identification of four main typologies (Table 1), from which individual representative case studies were selected for a deeper analytic study. These were then compared with the information collected from the literature, namely the models' manufacturing catalogues and the general information gathered for the state of the art presentation of the historical context [3,4,7].

Table 1. Main typologies of glass crystal models.

Typology	Brief Description	Models Quantity
A	Glass crystal model with textile lines inside, representing the crystal axes	63
B	Glass crystal model with interior model made of cardboard, representing the crystal axes	24
C	Glass crystal model with two rotating parts, showing the ability of the crystal to gain different forms	8
D	Glass crystal models that do not fit any of the characteristics mentioned above, probably due to improper restoration procedures	3

The careful and systematic examination and observation was also essential for the evaluation of the conservation condition of the collection, the definition of the main pathologies and problems observed and to be faced, as well as the selection of the paradigmatic case studies for a deeper analytical study. A comparative scale of three main deterioration grades was established for more precise conservation condition determination: (i) Poor conservation condition, where the glass is broken with missing parts, the interior thread lines or paper model are broken/ripped, and the paper adhesive tapes that join the glass edges are separating from the glass, weak, and failing on the adhesion to the glass; (ii) fair conservation condition, where the glass might be broken in some of the sides but no material is missing, the interior paper models or thread lines are not broken/ripped, and the paper adhesive tapes that join the glass edges might be lifting in some points, but the model integrity is not at risk; (iii) good preservation condition, where all the components seem to be complete and in place.

As mentioned before, 15 models were selected as being representative of the collection under study. The first criteria was to make sure that models from each of the four defined typologies presented in Table 1 were selected, six from A, six from B, one from C, and two from D. To have all the typologies was a way to also have access to all the materials that one can find on these models. As part of the choosing criteria, the conservation state of the models was also considered. The models in poor condition were preferred, since it is easier to collect samples and access to the interior materials in models that are less structurally cohesive. The selection contained nine models attributed to the Krantz company, five to altered models, and the only model that is proposed to be an in-house production (UL-DEP1249).

Concerning the selection and collecting of samples, the following materials were sampled: Small samples were collected from the inner paper/cardboard models, from the adhesive tapes (apparently made of paper or textile) that join together the glass faces of the crystal models (both fibers and adhesives were sampled), textile fibers from the interior axes lines, and paper labels (both paper fibers and adhesives were sampled). The sampling was performed by resorting always to areas where the exterior glass was broken, which enabled us to reach the interior paper models and textile axes. To sample the interior paper models and textile axes, the areas that presented damage were the preferred ones (for example, the ripped textile axes were the ones selected for sampling). Also, small samples of the papers and of the tapes were taken from unobtrusive areas of the artefact, along edges or previously damaged areas, and were prepared in identical way as the fibers' threads. Concerning the adhesives that were analyzed by means of FTIR-ATR, the principle of using damaged areas was also applied, using parts where the adhesive was loose and accessible and where the removal would not compromise the integrity of the object.

The first approach to a thorough characterization of the crystal models was made by means of a complementary multi-analytical approach, with the objective of chemical and molecular identification of the different materials that compose these models. The chemical and molecular characterization of the materials was mainly done by portable micro X-rays fluorescence (pXRF) or by collecting small samples to be further analyzed using optical microscopy (OM) and attenuated total reflectance Fourier-transform infrared (FTIR-ATR) spectroscopy.

The different threads and papers fibers found on the crystal models were analyzed by optical microscopy (OM). Different images were obtained with an Axioplan 2ie Zeiss microscope equipped with a transmitted and incident halogen light illuminator (tungsten light source, HAL 100); UV light (mercury light source, HBO 100 illuminator); and a digital Nikon camera DXM1200F, with Nikon ACT-1 application program software, for microphotographs. Samples were analyzed with 10× ocular lenses and 5×/10×/20×/50× objective Epiplan lenses (giving total optical magnification of 50×, 100×, 200×, and 500×). The small thread samples were taken from loose ends. Fibers were observed under the OM and identification was tried by using their morphological characteristics [8]. The fiber samples were prepared with distilled water and separated from one another with the help of a needle under a magnifying lens and then mounted on the microscope slide for longitudinal view from lowest to higher magnification, under simple polarized light and cross-polarized light [9]. Six samples of fibers were analyzed from a total of five models (type A, Table 1). The papers/textiles of the tapes were identified under the OM [10]. In total, 30 samples of fibers were analyzed, from a total of 15 models, on six different colored tapes.

Microchemical analysis by spot test was performed to very small samples of the inner paper/cardboard models (type B, Table 1) and to micro-samples of the paper labels that were present in all models. The phloroglucinol test was applied for lignin detection, using 1 g of phloroglucinol dissolved in a mixture of 50 mL methanol, 50 mL concentrated HCL, and 50 mL distilled water, taking into consideration TAPPI norms (T401 norm) [11]. The aluminon test was applied to check the presence of alum salts and a solution of 0.1 g aluminon in 1 liter of distilled water was prepared [12] (p. 12). The micro-samples were placed on a glass rod and a small drop of each solution was placed on different fiber samples, where the color change was checked with the help of a stereo binocular microscope. In the inner paper/cardboard models samples, the Raspail test was also tried for alum rosin detection, again, having in mind TAPPI recommendations (T408 norm) [13]. First, a drop of saturated sugar solution (about 35 g sucrose/20 mL water) was applied to the sample placed on the glass rod, allowed to soak for around three minutes, and the excess sugar solution removed with filter paper. It was followed by the application of one drop of sulfuric acid (96.6% H_2SO_4) on the sample and it was observed with the help of low-power magnification. The reaction should be immediate, and the color change may reveal the presence of alum rosin sizing [12] (p. 13).

Portable X-ray fluorescence spectroscopy (pXRF) was performed in situ, using Bruker S1 Titan Model 600, directly on the glass of the 15 models to determine the type of glass used to build the models. The spectra were acquired under the following conditions: The excitation source is a Rh target X-ray tube of 4 W, with maximum voltage of 50 kV and 100 μA, elemental range between Mg and U, and acquired with the integrated acquisition mode calibration GeoExploration, which operates at a 3-phase reading (90 s totally): Phase 1 at 30 kV, 26 μA; phase 2 at 50 kV, 26 μA; phase 3 at 15 kV, 26 μA (30 s each). Quantitative results were obtained with the automatic quantification proprietary software, Bruker Elemental S1. The elements, initially not presented in oxides, were then converted through oxide factors. To validate the obtained results, the glass standards from the Corning Museum of Glass, CMoG B and CMoG D, were analyzed under the same conditions [14] (p. 544).

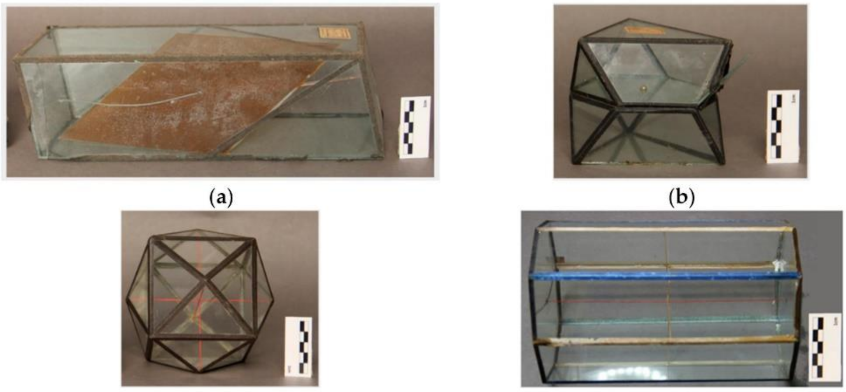
Samples of adhesives on tapes and on the glass surface were analyzed by infrared spectroscopy in attenuated total reflectance mode (ATR-FTIR). The spectra were acquired using an Agilent Handheld 4300 FTIR Spectrometer with a DTGS detector, with controlled temperature, and a diamond ATR sample interface; the analyses were performed at the sample surface. All spectra were obtained with a resolution of 8 cm^{-1} and 32 scans. Twenty adhesive samples were analyzed.

3. Main Results: Presentation and Discussion

3.1. Crystal Models Collection—Macro Observation

During the preliminary observation of the collection of crystal glass models, four main typologies were recognized (defined in Table 1), related to shape and main materials used. However, several other variations were observed. The paper adhesive tapes that join the glass are not the same for all the models. These came in different colors (black, blue, red, light yellow), different widths, and different textures (some look like a textile and others almost like a plastic material). The paper models inside the glass model can be all of the same color (white paper color) or can have two colors (alternated color sides: One of white paper color and the other of black glazed paper). The thread lines inside the glass models can have different colors, ranging between red, yellow, green, and orange. From the 98 models it was possible to identify one model with a cleavage interior plan on glass (Figure 3a).

For 13 of the models, the different features identified (either different colored paper adhesive tapes or the presence of plaster) can probably be related with latter interventions made overtime due to heavy usage of the objects. Also, it was noticed that four of the 98 models still reveal labels from the Krantz manufacturer.



(**a**) (**b**) (**c**) (**d**)

Figure 3. Krantz company glass crystal models from different generations: (**a**) Glass crystal model (UL-DEP1321) with inner glass cleavage plan; (**b**) glass crystal model (UL-DEP1309) with metal nuts for rotation; (**c**) glass crystal model (UL-DEP1240) with inner textile red lines; (**d**) glass crystal model (UL-DEP1280) with inner textile red and yellow lines; and blue, red, and black adhesive tapes.

Combining and analyzing the different characteristics mentioned above and comparing it with some catalogues from the Krantz company [7], it was possible to suggest a provenance for different kinds of models within the collection (Table 2).

Table 2. Proposal of provenance for the 98 models from Passos Manuel high school.

Model Reference	Provenience	Models Number
I	Possibly Krantz Company Models	85
II	Altered Models	12
III	Possibly in-house Manufactured Model	1

From the total 98 models, 85 are possibly from Krantz company, where early models reveal only black paper/textile adhesive tapes (Figure 3a) and later models have colored tapes (red and blue) (Figure 3b), and where the inner thread lines also changed from one color (Figure 3c) to several colors (Figure 3d) such as red, green, yellow, and orange. So, among these 85 models it is possible to notice the evolution of these characteristics and divide them into four distinct types that could represent four generations of glass crystal models made by the Krantz Company.

For the remaining 13 models of the Passos Manuel high school collection, it is not possible to recognize any characteristics from the Krantz models. However, as said before, most of these models appear to have been heavily altered.

As mentioned in the introduction, glass crystal models have a complex structure and the first methodological approach was also associated with the diagnosis of pathologies to estimate, through visual observation, the conservation condition of the collection comprising the 98 models. It is estimated that 23% of the models are in a poor conservation condition, mainly due to missing parts and lack of adhesion between materials. These models need an urgent intervention in order to avoid the loss of any important information.

Following these, 49% of the models are in a fair conservation condition, where no material is missing, and the model integrity is not at risk. These models might need some intervention but not at an urgent level.

Finally, 28% are in a good preservation condition, since all the components are in place and the models seem to be complete. These models do not need any remedial conservation. However, for an informed conservation decision and to implement correct preservation measures for the different parts composing the glass crystal models, further characterization of the materials is required.

3.2. Characterization of the Glass

The glass was analyzed by means of XRF, using a portable equipment in order to determine the glass chemical composition, which is shown in Table 3. By determining the glass compositional type, one can propose preventive conservation measures in a more informed way. Three points were analyzed for each model and the presented results are the average of those three measurements, together with the respective standard deviation. Only the major elements are presented and the data are normalized to 100%.

Table 3. Chemical composition of the glass from 15 crystal models, determined by pXRF, in weight percent of oxides.

Model Accession No.	Al_2O_3	SiO_2	K_2O	CaO	Fe_2O_3
UL-DEP1234	1.4 ± 0.3	83.5 ± 0.7	0.69 ± 0.02	14.17 ± 0.05	0.25 ± 0.01
UL-DEP1240	0.6 ± 0.2	89.5 ± 0.7	0.51 ± 0.02	9.27 ± 0.04	0.12 ± 0.01
UL-DEP1244	1.5 ± 0.2	85.4 ± 0.7	0.74 ± 0.02	12.15 ± 0.04	0.25 ± 0.01
UL-DEP1246	0.8 ± 0.2	90.9 ± 0.7	0.52 ± 0.02	7.53 ± 0.03	0.17 ± 0.01
UL-DEP1249	1.5 ± 0.3	83.8 ± 0.8	0.68 ± 0.02	13.78 ± 0.05	0.24 ± 0.01
UL-DEP1252	0.3 ± 0.2	82.1 ± 0.7	0.05 ± 0.01	17.30 ± 0.05	0.21 ± 0.01
UL-DEP1268	1.6 ± 0.3	84.3 ± 0.7	0.72 ± 0.02	13.06 ± 0.05	0.29 ± 0.01
UL-DEP1269	2.5 ± 0.3	81.4 ± 0.7	1.36 ± 0.02	14.49 ± 0.05	0.16 ± 0.01
UL-DEP1287	0.5 ± 0.2	83.6 ± 0.8	0.16 ± 0.01	15.48 ± 0.05	0.27 ± 0.01
UL-DEP1293	1.6 ± 0.2	84.4 ± 0.7	0.71 ± 0.01	13.01 ± 0.05	0.32 ± 0.01
UL-DEP1308	0.5 ± 0.2	83.4 ± 0.7	0.20 ± 0.01	15.67 ± 0.05	0.26 ± 0.01
UL-DEP1309	0.5 ± 0.2	85.1 ± 0.7	0.29 ± 0.01	13.87 ± 0.05	0.29 ± 0.01
UL-DEP1312	1.3 ± 0.9	84.2 ± 0.7	0.61 ± 0.02	13.63 ± 0.05	0.18 ± 0.01
UL-DEP1316	2.7 ± 0.3	84.2 ± 0.7	1.14 ± 0.02	11.55 ± 0.05	0.37 ± 0.01
UL-DEP1321	1.2 ± 0.2	81.4 ± 0.7	0.31 ± 0.01	16.84 ± 0.05	0.24 ± 0.01
CMoG B	5.2 ± 0.4	82.7 ± 0.7	1.15 ± 0.02	10.48 ± 0.04	0.43 ± 0.01
CMoG B (certified) [1]	5.7	81.4	1.31	11.18	0.44
CMoG D	6.2 ± 0.4	69.0 ± 0.7	11.37 ± 0.06	12.96 ± 0.05	0.45 ± 0.01
CMoG D (certified) [1]	6.1	63.5	12.93	16.93	0.59
CMoG B (certified) [2]	4.4	62.3	1.00	8.56	0.34
CMoG D (certified) [2]	5.3	55.5	11.30	14.80	0.52

[1] Certified values taken from: R. Brill, Chemical Analyses of Early Glasses, Vol. II, The Corning Museum of Glass, Corning (1999), p. 544. The certified values were normalized to 100% using only the oxides present in this table.
[2] Certifies values taken from the same reference without being submitted to any mathematical operation.

Analyzing Figure 4, where the contents of calcium oxide and potassium oxide are related and compared with the glass standards CMoG B and CMoG D, it is proposed that the glasses used to build the crystal models are of a soda rich type or soda-lime silica glasses, since these are located in the same area of the chart that the CMoG B standard (sodium rich or soda-lime silica standard) is located. The technique used to determine the glass chemical composition does not allow for the determination of the sodium oxide content, that being a light element usually needs an in vacuum set to be determined. The content of potassium oxide is in its majority below 1 wt%, which prevents the glass from being considered of a potassium rich composition or a mixed alkali composition [15]. Moreover, the contents of lead are all below 0.1 wt%, preventing the glass from being of a lead-rich type (lead contents above 25 wt%), supporting the proposed glass type.

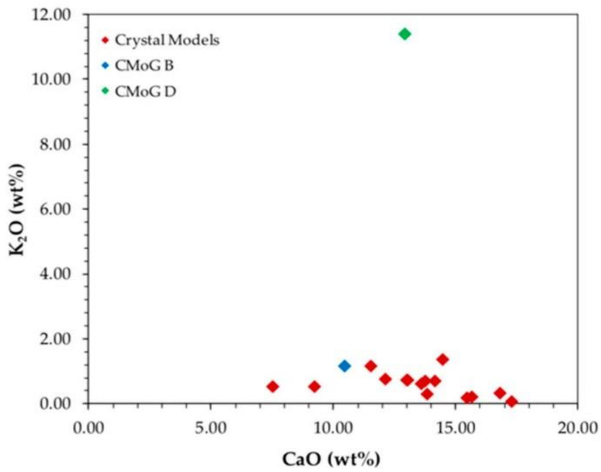


Figure 4. Binary plot of calcium oxide vs. potassium oxide, in weight percent of oxides and measured by pXRF.

3.3. *Characterization of Inner Paper/Cardboard Models and the Thread Lines*

Regarding the paper/cardboards microchemical testing (Table 4), the phloroglucinol spot test was negative except in one case (UL-DEP1249). This means that for one model only, the presence of lignin was found. The aluminon test for alum salts detection and Raspail test for alum rosin were both positive for all cardboard models. So, one can conclude that the model UL-DEP1249, which corresponds to the proposed in-house manufactured model, used very poor materials compared with the other analyzed models. The other models used lignin-free cardboards, although revealing also an acid source, due to the presence of rosin as sizing material.

Table 4. Microchemical tests on models with cardboard interior models.

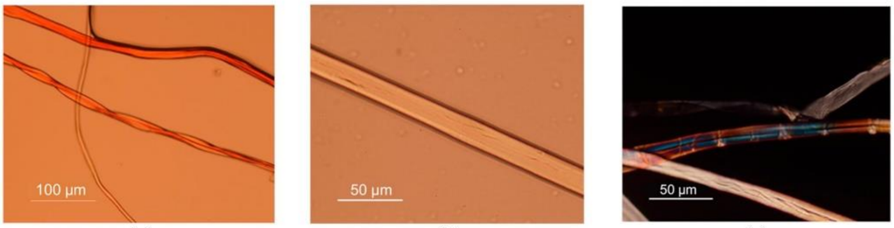
Model Accession No.	Phloroglucionol	Aluminon	Raspail Test
UL-DEP1249	Positive	Positive	Positive
UL-DEP1252	Negative	Positive	Positive
UL-DEP1287	Negative	Positive	Positive
UL-DEP1308	Negative	Positive	Positive

Through the observation of the inner line fibers (representing internal crystal axes) it is possible to notice that these are not a single type of fiber but a mixture of fibers. The observation under the OM and the comparison of the images with the database of Conservation and Art Materials Encyclopedia (CAMEO) and the literature [9,11], allows one to suggest the presence of cotton, a flat fiber with ribbon-like appearance revealing twisted areas, thick walls, and small lumen under the microscope (Figure 5a); wild and cultivated silk with a smooth appearance and lustrous filaments (Figure 5b) and even traces of flax or hemp with the presence of lines going across the fiber; and forming cross hatching and knots, plus a narrow lumen (Figure 5c).

3.4. *Paper Labels*

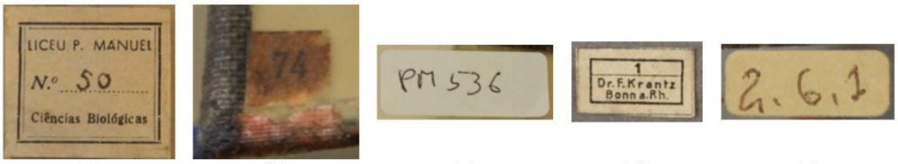
Most of the glass crystal models studied presented three labels: The label from Liceu Passos Manuel (Figure 6a), which corresponds with a list of the names from the different crystal representations; smaller labels (Figure 6b), for which correspondence is still undetermined; and labels from their tumble (Figure 6c), a number attributed to each artefact of the collection when entered into the museum.

As mentioned before, apart from these three labels, there are labels from the Krantz company (Figure 6d) present in four different models, and a few other different types of labels (Figure 6e), such as labels with names or numbers, with no matching correspondence determined so far.



(a) (b) (c)

Figure 5. Fibers under optical microscope: (**a**) Red inner textile line from UL-DEP1316 model (cotton); (**b**) beige inner textile line from UL-DEP1312 model (silk); (**c**) beige inner textile line from UL-DEP1268 model (flax or hemp).



(a) (b) (c) (d) (e)

Figure 6. Labels present in the glass crystal models: (**a**) Liceu P. Manuel; (**b**) smaller labels with no given correspondence; (**c**) tumble number; (**d**) Krantz company; (**e**) other labels.

Over time, these kinds of labels become a historic part of the objects, with irreplaceable information, therefore their preservation is an important concern for the intervention of the entire object [16]. For that reason, it is important to observe the different labels and understand their historic and cultural significance, namely trying to determine which ones have this meaning and which have not, as well as to characterize their composition stability. From the labels described in the previous paragraph, the only one that was not considered historic was the tumble label, since these were attached to the models in a chronological line that does not yet correspond to an historical moment.

At that stage, the microchemical tests of phloroglucinol and aluminon were performed on all the labels deemed as historic and the results are presented in Tables 5 and 6, respectively.

Table 5. Phloroglucinol microchemical tests on different paper labels.

Model Accession No.	Liceu P. Manuel	Smaller Labels	Krantz	Other Labels
UL-DEP1240	-	-	-	Negative
UL-DEP1249	-	-	-	Positive
UL-DEP1252	Negative	Positive	-	-
UL-DEP1287	-	-	-	Negative
UL-DEP1293	Negative	Positive	-	-
UL-DEP1308	Negative	Positive	-	-
UL-DEP1309	-	-	Negative	-
UL-DEP1321	Negative	-	-	-

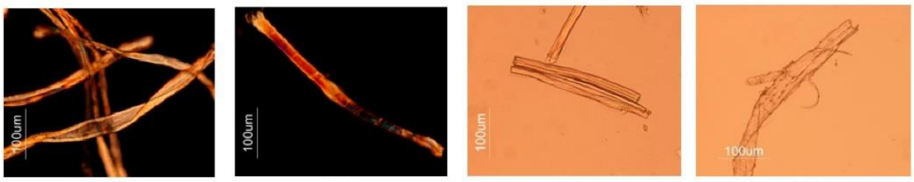
Results were consistent for each type of label, apart from the category 'other labels', which revealed some inconsistent results. Analyzing each type of label separately, the paper revealing the best quality was the one from the Krantz company, due to the absence of lignin (phloroglucinol test) and alumen (aluminon test). The Liceu P. Manuel labels also presented good quality, based on the absence of lignin and despite the presence of alum salts; the small labels represented a concern, since the presence of lignin (phloroglucinol test was positive) will cause acidic hydrolysis of the paper and its dislocation and chemical and physical alteration, already visible by its color appearance. These labels did not reveal alum salts, but the presence of lignin indicates mechanical wood pulp production and therefore, acid hydrolysis deterioration. Finally, the 'other labels' did not present consistent results, alternating between good and bad quality.

Table 6. Aluminon microchemical tests on different paper labels.

Model Accession No.	Liceu P. Manuel	Smaller Labels	Krantz	Other Labels
UL-DEP1240	-	-	-	Negative
UL-DEP1249	-	-	-	Positive
UL-DEP1252	Positive	Negative	-	-
UL-DEP1287	-	-	-	Positive
UL-DEP1293	Positive	Negative	-	-
UL-DEP1308	Positive	Negative	-	-
UL-DEP1309	-	-	Negative	-
UL-DEP1321	Positive	-	-	-

3.5. Adhesives and Constructive Tapes

Observing the fibers from the adhesive tapes under the OM and comparing it with the mentioned literature, it is possible to identify different types of fibers. A mixture of cotton and other fibers could be identified through the presence of its characteristic, such as a ribbon-like appearance revealing twisted areas for cotton (Figure 7a), lines going across the fiber and forming cross hatching and knots for flax or hemp (Figure 7b), and longitudinal lines for jute fibers (Figure 7c). In the samples observed, textile cotton fibers seem dominant. The only tape where it was possible to identify the presence of a softwood fiber showing sequenced pits and other species' features, such as ray parenchyma (Figure 7d) was in the black tape of the model UL-DEP1234, being that this was the item that was heavily repaired, so this came probably from a latter intervention.



(**a**) (**b**) (**c**) (**d**)

Figure 7. Fibers under the optical microscope: (**a**) Cotton sample from UL-DEP187 model; (**b**) flax or hemp sample from UL-DEP1312 model; (**c**) jute sample from UL-DEP1268 model; (**d**) softwood sample from UL-DEP1234.

The adhesives and constructive tapes were also analyzed by means of ATR-FTIR, resorting to the use of a portable equipment to make the molecular characterization. From the 20 samples of adhesives analyzed by means of ATR-FTIR, seven were identified as protein based glue, four as protein glue and cellulose, two as cellulose, and in five of the samples other components were identified. These last five samples contained protein, cellulose, and materials that were identified as gypsum, kaolin, Arabic gum, and shellac. In two other samples the presence of poly(vinyl acetate) (PVAc) was also identified. The presence of these last mentioned materials is probably the result of some changes made by the school professors, or other professionals, during the period of use of the models, with the objective of making the necessary repairs for the models to become useful and usable again.

In Figure 8, spectra from three samples collected from different parts of the models UL-DEP1308 and UL-DEP1309 are presented. Spectrum (a) was collected from model UL-DEP-1308, from an edge of glass without paper adhesive tape and spectrum (b), which came from the same model, was removed from a glass face near a paper adhesive tape. Spectrum (c) was collected from model UL-DEP1309, from a glass edge that had no contact with paper adhesive tape. Two types of materials were identified: protein (b), cellulose (c), and the mixture of the two (a). Protein spectra are typically recognized by the presence of the carbonyl group belonging to the amide I (here at 1630 cm^{-1}) and of amide II (1536 cm^{-1}). These, along with a third one, usually named by amide III (at 1454 cm^{-1}), form the characteristic stair-step pattern. Being coupled with the N-H stretching band (centered at ca 3275 cm^{-1}), it is possible to confirm the presence of the amide, and so, the protein [17]. Therefore, it is possible to infer that one of the present adhesives might be some type of protein glue, despite being impossible to further determine which adhesive it is.

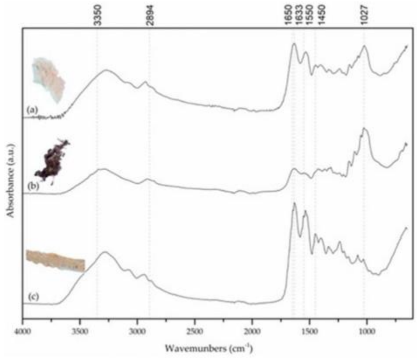


Figure 8. ATR-FTIR spectra of (**a**) protein and cellulose from UL-DEP1308 model; (**b**) cellulose from UL-DEP1309 model; and (**c**) protein sample from UL-DEP1309 models.

Cellulose spectra can be recognized by two regions of absorbing bands, first between 3660–2800 cm^{-1} and second at 1650–400 cm^{-1}. The first region is characterized by the stretching vibration of the hydroxyl group (centered at 3290 cm^{-1}) and the band attributed to CH stretching vibration of the hydrocarbon groups in polysaccharides (ca 2915 cm^{-1}). The second region comprises the vibration band of water (ca 1637 cm^{-1}) and bending vibrations of CH and COH (at ca 1428, 1367, 1334 cm^{-1}), and the COC stretching vibrations (1027 and 896 cm^{-1}) [18]. The presence of cellulose is probably due to contamination of the sample, being that this sample came from an adhesive tape. The presence of softwood, which can be seen on the samples of the model UL-DEP1308, spectrum (a) probably justifies the two components, protein and cellulose.

In the spectrum presented in Figure 9, the presence of PVAc was identified among the adhesives used in the glass crystal models of the collection. This sample was collected between the paper adhesive tape and the glass edges. Among the 15 models selected as being representative of the collection of 98 models, this is one of two models that have PVAc, with the second one colored in black, perhaps to match the color of the tape where it was applied. This type of adhesive is identified by the presence of the strong C=O (at 1729 cm^{-1}) and C–O–C (1224 cm^{-1}) stretching vibration bands related with the acetate ester, along with two less intense peaks of CH_3 asymmetric and symmetric bending bands (at 1433 cm^{-1} and 1370 cm^{-1}, respectively). Additionally, there is also an antisymmetric stretching vibration of CH_3 (2973 cm^{-1}) [18].

In some models it was possible to identify other materials (Figure 10) such as gypsum, Arabic gum, shellac, and kaolin, and these samples were collected from around the smaller label (Arabic gum), from an adhesive tape (kaolin) where Arabic gum was also present, and from edges of glass without adhesive tape (gypsum and shellac).

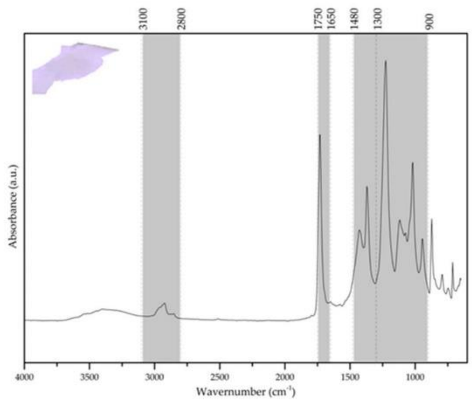


Figure 9. ATR-FTIR spectrum of poly (vinyl acetate) (PVAc) from sample of UL-DEP1287 model.

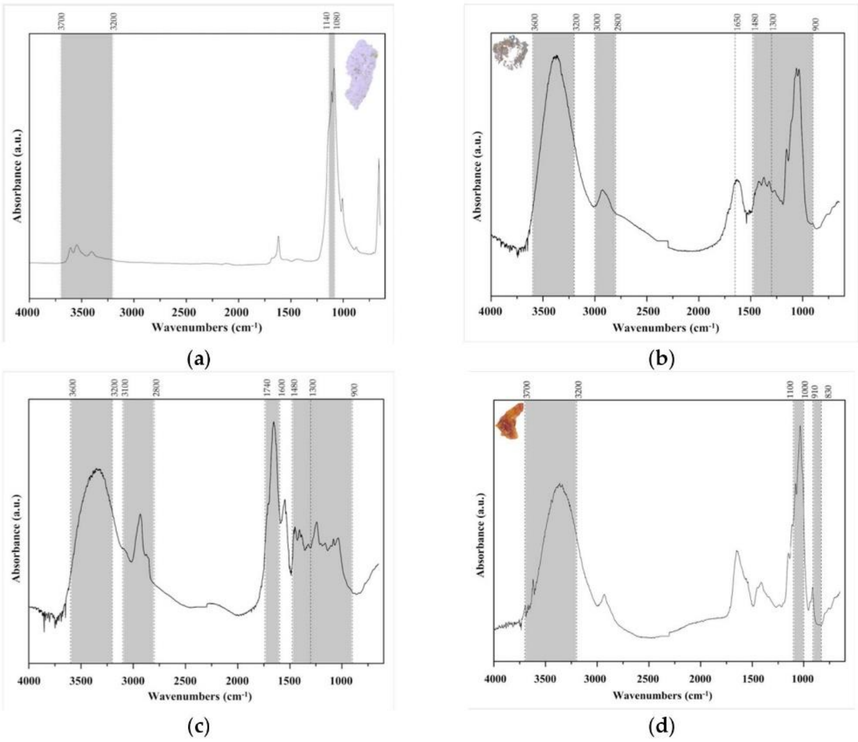


Figure 10. ATR-FTIR spectrum of (**a**) gypsum from sample of UL-DEP1316 model; (**b**) Arabic gum from sample of UL-DEP1308; (**c**) shellac from sample of UL-DEP1269; (**d**) kaolin from sample of UL-DEP1316.

Gypsum (Figure 10a) is generally identified by having an asymmetric SO_4^{3-} stretching band between ca 1140–1080 cm^{-1} and an antisymmetric and symmetric OH stretching band [17]. Arabic gum (Figure 10b) is identified by the OH stretching band between ca 3600–3200 cm^{-1}, CH stretching band between ca 3000–2800 cm^{-1}, OH bending band at ca 1650 cm^{-1}, CH bending band between ca 1480–1300 cm^{-1}, and finally CO stretching bands between 1300–900 cm^{-1} [17]. Shellac (Figure 10c) presents the typical bands at five different regions, the OH stretching band at ca 3600–3200 cm^{-1}, CH stretching bands at 3100–2800 cm^{-1}, C=O stretching band at ca 1740–1640 cm^{-1}, the CH bending bands at ca 1480–1300 cm^{-1}, and the CO stretching bands at ca 1300–900 cm^{-1} [17]. Finally, kaolin (Figure 10d) is identified by the OH stretching band at ca 3700–3200 cm^{-1}, the asymmetric Si–O–Si stretching band at ca 1100–1000 cm^{-1}, and SiO stretching at ca 910–830 cm^{-1} [17].

The presence of the different materials mentioned above, gypsum, kaolin, Arabic gum, and shellac, along with the presence of PVAc, strengthen the hypothesis that the models suffered alterations and repairs that became necessary with time and use.

4. Discussion

Since the glass sheets that compose the models do not show bubbles or any signs of having been blown, relating these observations with the chronology of the models, it is proposed that these were made using float glass. Float glass (also known as window glass) is an industrial process of glass sheets production, where the molten glass is pushed to a molten bath of tin. The glass will then float on the tin and be placed in an annealing kiln until it reaches room temperature. The result is a glass sheet with no bubbles and invisible imperfections to the naked eye. Moreover, the sheets are perfectly plan on both sides, the side that floated on the tin and the other side that is turned to the atmosphere. Relating this with the composition that is proposed, a soda-lime silica type, it is possible to estimate that the glass is not very susceptible to degradation, being a fairly stable composition. Having in mind the glass degradation process, one can for instance compare it with a composition rich in potassium (instead of sodium), which would present a composition much more susceptible to degradation under the same conditions, due to the atomic radius of the potassium ion. Briefly recalling the glass degradation, the first reaction to occur is the ionic exchange, where alkaline ions, negatively charged, are extracted from the glass matrix forming a sodium or potassium hydroxide solution. In order to maintain the matrix neutrality, these leached ions are replaced by H_3O^+ ions [19,20]. K has an atomic radius bigger than the one of Na, meaning that when the glass has the same composition, changing only the alkali ion (K or Na), for each leached potassium ion, more H_3O^+ ions will fit into the glass matrix, since K occupied a bigger space than Na [21]. Moreover, the calcium oxide content, which was estimated as above 10 wt% for all analyzed glasses, acts as a matrix stabilizer (property modifier), contributing to the glass' resistance to degradation [22]. No crystals or iridescent areas were observed on the glass sheets.

Considering now the papers and carboards used on the crystal glass models, they belong to the first full industrial era of paper production, where dangerous materials such as lignin and rosin alum would be expected to be found. In fact, machine made papers from late nineteenth and early twentieth centuries are usually of very poor quality, due mainly to material composition. In the first studies on the deterioration of paper, in Germany, following the creation of the first laboratories for paper testing in 1884, the presence of lignin was classified as one of the main intrinsic causes of the deterioration of the industrial paper. Later, in the 1920's, researchers in Switzerland identified the presence of acidic salts of alum in paper as another of these causes [23,24]. These substances act as catalysts for acid hydrolysis, one of the main degradation phenomena of cellulose. The reaction contributes to the breakdown of the polymer chain, affecting the glycosidic bonds that link the glucose units of the cellulose. This results in the formation of acids, which catalyze the hydrolysis, becoming a continuous process of cellulose degradation [25,26]. In fact, the phenomenon affects even better quality paper, being intrinsic to the aging and deterioration of cellulose and being dependent on external factors such as environmental conditions and storage [24]. However, the main results reveal the choice of reasonable quality papers for the model's production. This can be proven by the presence of lignin free papers. Even so, the presence of alum salts and rosin sizing, especially in the cardboard models, is a real concern, increasing the risk of deterioration by acid hydrolysis and its collapse over time inside the glass crystal model.

When thinking about the preventive conservation measures for these objects, a problematic issue stands out: how to create preventive conservation measures that serve both glass and paper? Glass, an inorganic material, needs to be kept in a controlled environment of around 45% +/− 5% of relative humidity (RH), and it should never be submitted to extreme RH fluctuations [27]. The temperature does not represent a big concern, unless it affects the RH, and in relation, light and lighting systems are not a problem, unless these warm up too much. Moreover, the storage and display locations or cabinets should be ventilated to prevent heat and dust accumulation [27]. Concerning the chemical nature of the environment, this should be as neutral as possible. If the environment is an acidic one, the corrosion mechanism will be accelerated and the alkali leaching deepened from the glass matrix. The acid will be a H^+ source, this way accelerating and deepening the corrosion process. Different acid environments were tested and formic acid, specifically, was determined to be the second factor (after water) to have in mind when dealing with glass conservation [20,28]. On the other hand, if the environment is alkaline, especially with a pH above 9, the silica network dissolution will occur. The silica network dissolution corresponds to the breakdown of siloxane bonds existent on the glass/solution interface [20].

Looking now to paper, in terms of preventive conservation, stable and lower relative humidity are also recommended, but in that case high temperature and light are also important factors of cellulose degradation, accelerating acid hydrolyses but also causing photodegradation and oxidation processes [29,30]. As it was seen before, paper degradation can lead to an acidic environment, which can be very dangerous to glass, accelerating its degradation process. Usually, paper also needs and benefits from an alkali reserve, but not higher than pH 9, which also leads to degradation processes, such as alkaline hydrolyses and cellulose peeling-off reaction [29]. As seen above, this would also be dramatic to glass, since atmospheres with pH above 9 will cause the silica network dissolution. On the other hand, recalling the primary stage of glass degradation, alkali ions will be leached from the glass matrix. So, optimal preventive conservation conditions necessary for glass and paper are compatible, but what are incompatible are the aging degradation processes of each material that develop in opposite ways. However, can the alkali ions freed from the glass be enough to neutralize the acidic species unleashed by aged paper? If so, inside the glass models a favorable microclimate will be created, where the general atmosphere is neutral. The materials will end up reaching an equilibrium point maintaining a neutral environment that suits the conservation of both materials. This is a proposal that needs more research to verify the premise, however, if this ends up being the situation, the conservators need only to monitor the external environment of the models and prevent drastic changes in the temperature and RH so that the internal balance is not disturbed.

Looking to the apparent stability of the models under study, both the inner paper/cardboard of the inner models that although having rosin size, a source of acidity, still maintains its resistance and of glass without visible signs of strong chemical deterioration, this theory seems to make sense and justifies further investigations. In fact, main deterioration processes: (i) Of the glass, concerns physical deterioration from handling and poor storage; (ii) of the paper, concerns a natural yellowing that may have been caused by light-induced degradation and already some acid hydrolysis caused by the presence of rosin in the paper matrix. The water line stains also visible on the paper/cardboard models may be caused by fluctuations of the environmental conditions and formation of water condensation on the glass, which caused these stains on the paper. Other biodegradation and physical deterioration were probably mostly caused by poor handling and poor storage conditions of recent years, where the models had no regular use.

Considering now the labels as part of the historic evidence of the trajectory of these models and recognizing the importance of their safeguarding, the ones possible to identify, such as the Passos Manuel high school and Krantz company, revealed themselves of fair and good quality. However, it is important to be aware that the small labels composed by very poor materials may not last long, unless some remedial conservation is done to neutralize them. It is not known when and why these labels were attached to the glass models, but at least a good record of their existence should be done as soon as possible. The same with the so called 'other labels', some of poor quality, that have a number record, which in the future may solve historians' doubts. Fortunately, in that case, acids are not trapped inside the model. So, label composition versus degradation processes of glass are less relevant. But it is always a concern for the general environment and may be for the interface layer between the glass surface and the label, but here there is also the adhesive layers to be considered.

Looking to the results obtained from the analysis performed on the adhesives collected from the exterior tapes that join the glass faces of the crystal models, the majority of the adhesives proved to be of a protein nature. In terms of conservation, protein adhesives can suffer biodeterioration attacks, and depending on the adhesive, these can lose their integrity and adhesive power with age and under certain conditions such as very high or very low RH% and temperature. Some of the tapes are already detaching from the glass, which can be a sign that the adhesives are not entirely fulfilling their function. Tapes in general are of good quality, revealing cotton fibers as its main composition. As far as the authors could evaluate, no signs of biodeterioration was identified. However, the need for short period monitoring becomes clear, since the protein adhesives may lose their adhesive power, which will result in the collapse of the entire system of the model. Concerning these materials, there is not much a conservator can do to prevent their falling, apart from a close monitoring and control of the surrounding environment. The identification of materials that, at a first analysis, are believed to be the result of alterations or interventions made on the models to keep them usable, are also important to show the diversity of materials that the conservator has to deal with when thinking about preventive conservation measures for these objects.

5. Conclusions

This work aims to be a preliminary approach to the study and characterization of glass crystal models and the materials that are part of their construction. As far as the authors are aware, this is the first systematic and full material study of these types of artefacts that are part of the 20th century legacy of the teaching methods for science and it allows for the understanding of the practices in classes and facilities available in the Portuguese schools, an important subject for the history of science.

The first part of this work was dedicated to the research on the history of these models to understand their origins and creation purposes. This will also be a great contribution to raise the value of this heritage and to open the possibility for other studies concerning these type of artefacts. It was interesting to realize that a large part of the collection, still in a good conservation state, was probably acquired from the Krantz company. The fairly well preserved objects reveal continuous care by the main users of these artefacts. Another interesting aspect was the finding of a probably in-house built model. What was the reason for the creation of this model? Was it a common one or does it reflect the creation of a new type of crystal not yet available in the commercial sector? Were there any financial difficulties faced by the Portuguese education system? So many questions can be asked after this find. However, we are now aware that it must be preserved as a unique piece and that increases its value for the history of science and education. Nevertheless, the materials used to build it are of a poor quality compared with the other models, so it is a conservation challenge to be faced by the conservation team.

The analytical approach proved to be appropriated for the materials' characterization: With pXRF it was possible to determine that the glass is of a soda-lime glass type and the observation under the optical microscope allowed for the identification of the fibers present in the threads from the inner axes and the fibers from the constructive tapes, and for both a mixture of fibers were identified, such as cotton, flax or hemp, and jute. The microchemical tests performed on the cardboard from the interior models revealed the presence of alum salts, alum rosin, and the absence of lignin, which shows a fair–good quality for the paper/cardboard. Finally, ATR-FTIR was used to characterize the adhesives found in the constructive tapes joining the glass sheets. Protein and cellulose were identified as the main adhesives for the majority of analyzed samples.

The material characterization revealed that the main components that constitute the models are of a reasonably good quality, proving to be stable. However, despite the materials' quality and stability, the main components, glass and paper, have degradation processes that develop in opposite ways. Paper degradation can lead to an acidic environment, which can be very dangerous to glass, accelerating its degradation process. As said before, usually, paper also needs and benefits from an alkali reserve but not higher than pH 9, which also leads to degradation processes. Further research is needed to understand if alkali ions freed from the glass are enough to neutralize the acidic species unleashed by aged paper, which would result in a neutral atmosphere inside the glass models. That way, a favorable microclimate would be created inside the glass models, being of paramount importance to keep the external environment stable not to disturb the internal equilibrium. As already mentioned, further research is needed to understand the implications of the combination of the degradation processes of these two materials.

This first approach to the study of these models will serve as a base of knowledge for the development of preventive conservation measurements for these types of models and the identification of the main conservation issues concerning this cultural heritage. As future work, guidelines will be developed for schools, museums, and other institutions that will help these establishments in the preservation of their collections.

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Appendix II – p-XRF glass results

Table 9. Chemical composition of the glass from glass crystal models, by p-XRF, in weight percent of oxides (% wt.)

Accession No.	Al_2O_3	SiO_2	K_2O	CaO	Fe_2O_3
UL-DEP1234	1.4 ± 0.3	83.5 ± 0.7	0.69 ± 0.02	14.17 ± 0.05	0.25 ± 0.01
UL-DEP1240	0.6 ± 0.2	89.5 ± 0.7	0.51 ± 0.02	9.27 ± 0.04	0.12 ± 0.01
UL-DEP1244	1.5 ± 0.2	85.4 ± 0.7	0.74 ± 0.02	12.15 ± 0.04	0.25 ± 0.01
UL-DEP1246	0.8 ± 0.2	90.9 ± 0.7	0.52 ± 0.02	7.53 ± 0.03	0.17 ± 0.01
UL-DEP1249	1.5 ± 0.3	83.8 ± 0.8	0.68 ± 0.02	13.78 ± 0.05	0.24 ± 0.01
UL-DEP1252	0.3 ± 0.2	82.1 ± 0.7	0.05 ± 0.01	17.30 ± 0.05	0.21 ± 0.01
UL-DEP1268	1.6 ± 0.3	84.3 ± 0.7	0.72 ± 0.02	13.06 ± 0.05	0.29 ± 0.01
UL-DEP1269	2.5 ± 0.3	81.4 ± 0.7	1.36 ± 0.02	14.49 ± 0.05	0.16 ± 0.01
UL-DEP1287	0.5 ± 0.2	83.6 ± 0.8	0.16 ± 0.01	15.48 ± 0.05	0.27 ± 0.01
UL-DEP1293	1.6 ± 0.2	84.4 ± 0.7	0.71 ± 0.01	13.01 ± 0.05	0.32 ± 0.01
UL-DEP1308	0.5 ± 0.2	83.4 ± 0.7	0.20 ± 0.01	15.67 ± 0.05	0.26 ± 0.01
UL-DEP1309	0.5 ± 0.2	85.1 ± 0.7	0.29 ± 0.01	13.87 ± 0.05	0.29 ± 0.01
UL-DEP1312	1.3 ± 0.9	84.2 ± 0.7	0.61 ± 0.02	13.63 ± 0.05	0.18 ± 0.01
UL-DEP1316	2.7 ± 0.3	84.2 ± 0.7	1.14 ± 0.02	11.55 ± 0.05	0.37 ± 0.01
UL-DEP1321	1.2 ± 0.2	81.4 ± 0.7	0.31 ± 0.01	16.84 ± 0.05	0.24 ± 0.01
CMoG B	5.2 ± 0.4	82.7 ± 0.7	1.15 ± 0.02	10.48 ± 0.04	0.43 ± 0.01
CMoG B (certified)[8]	5.7	81.4	1.31	11.18	0.44
CMoG D	6.2 ± 0.4	69.0 ± 0.7	11.37 ± 0.06	12.96 ± 0.05	0.45 ± 0.01
CMoG D (certified)[8]	6.1	63.5	12.93	16.93	0.59
CMoG B (certified)[9]	4.4	62.3	1.00	8.56	0.34
CMoG D (certified)[9]	5.3	55.5	11.30	14.80	0.52

[8] Certified values taken from R. Brill, Chemical Analyses of Early Glasses, Vol. II, The Corning Museum of Glass, Corning (1999), p.544 [21]. The certified values were normalized to 100% using only the oxides present in this table.
[9] Certifies values [21] taken without being submitted to any mathematical operation.

Appendix III – Float glass production

Invented in the 50s, float glass appeared due to the need of an economic methodology for flat glass fabrication for automotive and architectural applications [32]. The process involves of making a piece of glass float on a bath of melted tin, which creates a smooth surface naturally [32]. Figure 16 presents the process of fabrication of float glass.

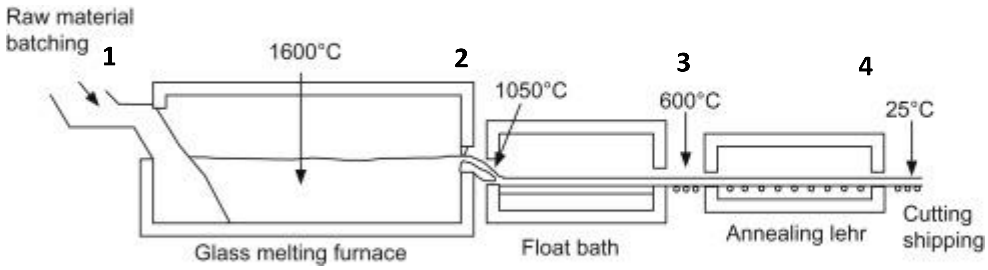

Figure 16. Process of float glass production

The process of float glass fabrication is comprised by the following steps [32]:

1. The raw materials to produce a soda-lime-silica glass are melted in a glass melting horizontal furnace that, to achieve a good chemical homogeneity, should be at a temperature between ≅ 1550°C and 1600°C [32];
2. When transitioning to the float bath state, the temperature is brought to between 1100°C and 1200°C and the allowed to flow into a refractory channel to a molten tin bath at an even lower temperature, around 1050°C. At this temperature, soda-lime-silica glass is less dense (≅ 2.3 g/cm^3) than tin (≅ 6.5 g/cm^3); this is the reason why this type of glass is used in this process [32];
3. The soda-lime-silica glass is then subjected to cooling and annealing processes, which occur from temperatures around 600°C down to 25°C [32];
4. The last phase is to produce uniform sheets of glass with thickness of 125 mm and flattening the surfaces [32].